SUPPLEMENTARY INVESTIGATIONS
OF
INFRA-RED SPECTRA

Part V—Infra-Red Reflection Spectra
Part VI—Infra-Red Transmission Spectra
Part VII—Infra-Red Emission Spectra

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PREFATORY NOTE.

The present volume contains supplementary data on doubtful points, which arose in connection with the preceding work on infra-red spectra. The various phases treated, except Part VII, Chapter I, (4) and (5), and Chapter II, were ready for publication during the summer of 1907, when through the generosity of the Carnegie Institution of Washington it was made possible to combine all the material into a new volume, which was then delayed for the additional data on emission spectra of metal filaments and insulators, thus rounding up the subject as completely as is possible at this time. This completes, for the present, the "program of investigation." The subject, however, is not exhausted — not even thoroughly initiated — for we know but little more of the cause of absorption and of emission lines and bands, other than those due to several well-known groups of atoms, than we did twenty years ago, when Julius and Ångström, independently, examined infra-red spectra. Each renewed effort is a step in advance, as the present data on the effect of molecular weight illustrate. The main problem is to obtain suitable material, which seems to be partly a matter of chance. For example, one of the first substances ever examined for selective reflection was quartz. It is the easiest obtainable, and it illustrates the question of selective reflection better than any other substance yet found, save carborundum, which was one of the latest minerals to be examined. On the other hand, after examining over 300 different substances, it has remained until the very last to find a series that so well illustrates the effect of molecular weight as the data on the carbonates herewith presented. The reflection spectra of the carbonates and nitrates in solution deserve further study. They are easily obtainable, and their reflection bands, which are strong, lie in the region of the spectrum where the radiation is quite intense, so that no serious difficulty need be anticipated. Colloidal metals also deserve further attention. Artificial substances, except carborundum, have never been examined, and it is intended to make a study of the silicides, provided they can be melted into homogeneous masses.

In Part III (Carnegie Publication No. 65) the discussion of the accuracy attainable refers to the region up to about 12 μ. Beyond this point the absorption of the rock-salt prism increases very rapidly, and it was not possible to attain great accuracy. In fact, the writer has given but little weight to his isolated observations lying beyond 14 μ, although others have been able to verify them, a notable example being calcite (Carnegie

Publication No. 65, p. 70), where the probability of a band at 14 μ is based upon two spectrometer settings and only three observations.

In Carnegie Publication No. 65, Appendix V, "Note on Blowing Quartz Fibers," the originator of the method was then unknown to the writer. Since then it has been found that in addition to shooting quartz fibers the method of blowing them is fully described by Boys in the London Electrician, p. 220, Dec. 11, 1896, "Blowing and Shooting Quartz Fibers."

Prof. E. F. Nichols has written me that he found the method in 1891, and exhibited it at the jubilee celebration of the Physikalische Gesellschaft in Berlin in 1896.

In Carnegie Publication No. 35, p. 51, line 10 from the bottom should read: "Carbon dioxide is the only gas studied which has no strong absorption bands except at 4.5 μ and 14 μ."

W. W. Coblentz.

Washington, D. C., *May*, 1908.

PART V.

INFRA-RED REFLECTION SPECTRA.

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CHAPTER I.

INTRODUCTION.

In the preceding volume, Part IV, the reflection spectra of several groups of chemically related minerals were examined, including sulphates, sulphides, and an extensive group of silicates. This examination did not include the oxides and carbonates which were not obtainable at that time. To examine the substances in chemically related groups seemed to be the only logical way to gain insight into the mechanism of selective absorption and of selective reflection. The main difficulty lay in obtaining material of sufficient size to produce a suitable reflecting surface. A list of minerals, which occur in sufficient size and homogeneity, was sent out to various mineral dealers who very kindly submitted several large boxes of specimens for selection. Even after this first elimination it was possible to obtain only about 10 per cent of the number of minerals desired. In addition to these minerals a considerable number of specimens were selected from the collection in the U. S. National Museum.

The apparatus and methods employed were essentially the same as in the preceding investigation. The spectrum was produced by means of a rock-salt prism, and mirror spectrometer previously described. The reflecting power of the mineral was compared with that of a silver mirror. The surfaces were ground plane, but were not always of the highest polish. Since primarily we are only concerned with the accurate location of bands of selective reflection, the question of polish is of secondary importance.

The spectrometer slits were 0.3 mm., or about 2′ of arc, as in the preceding work. The radiation from a Nernst "heater" was projected upon the reflecting surfaces by means of a mirror having a focal length of 15 cm. and an aperture of 12 cm.

The reflection spectrum was explored by means of a Rubens thermopile. Although its sensitiveness was greater than the radiometer used previously, the unsteadiness at times, due to magnetic disturbances, necessitated repeating the observations at each spectrometer setting. When using the radiometer, it was rarely necessary to repeat the observations in exploring the spectrum up to 9 or 10 μ, while in the present work, using a thermopile, the region beyond 9 μ was examined under the greatest difficulties, and in the case of the carbonates no attempt was made to locate the band at 11.4 μ. When the reflection faces were less than the standard size, 2 by 3 cm., which was frequently the case, the silver comparison mirror and the specimen were covered with diaphragms having equal openings, so that equal areas of the two surfaces were exposed.

CHAPTER II.

INFRA-RED REFLECTION SPECTRA OF VARIOUS SUBSTANCES.

CARBONATES.

SMITHSONITE ($ZnCO_3$).

(Stalactitic crystalline mass. From New Jersey. Curve *a*, fig. 1.)

The specimen examined was highly polished. The reflection curve is strong, and is a complex of two bands, as will be noticed in nearly all the carbonates examined. The maxima occur at 6.65 and 7.05 μ.

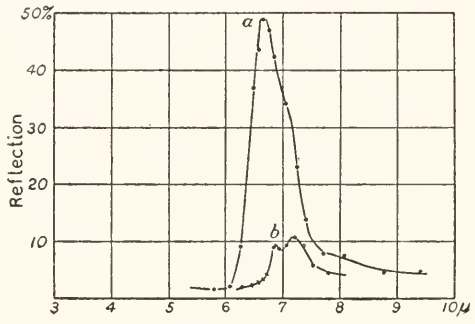

FIG. 1. — Smithsonite (*a*); Cerussite.

There seems to be a silicate calamine ($H_2O \cdot 2ZnO \cdot SiO_2$) having the same name. In fact the sample was purchased as a silicate. The present examination shows that the specimen examined is the carbonate known by that name. In other words, this is an independent method of analyzing such a mineral.

CERUSSITE ($PbCO_3$).

(From New South Wales. Curve *b*, figs. 1 and 2.)

This is a rare mineral and the present specimen was a fragment having a surface about 1.5 by 2 cm. The surface itself was corrugated, with several plain highly polished plates about 2 by 15 mm. It was the only specimen obtainable and no risk was taken in attempting to grind it. The reflection curve *b*, fig. 1, therefore does not indicate the true reflecting power. The individual bands, however, are well resolved, the maxima being at 6.9 and 7.25 μ. In fig. 2, curve *c*, the reflection curve is drawn on a larger scale, which emphasizes these maxima.

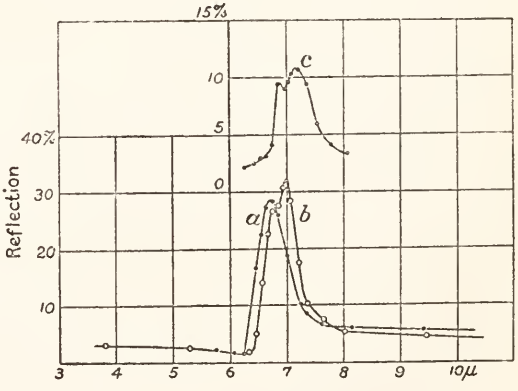

FIG. 2. — Strontianite (*a*); Witherite (*b*); Cerussite.

STRONTIANITE ($SrCO_3$).

(Massive specimen. From Hamm, Westphalia, Germany. Curve *a*, fig. 2.)

The specimen examined had a large, well-polished reflecting surface. As in all the carbonates studied the height of the maximum reflection is only about 30 per cent. This is the only carbonate examined which has but one reflection maximum, which is at 6.74 μ. It will be noticed presently that these maxima shift toward the long wave-lengths with increase in molecular weight. Since the intensity of the two bands is unequal, it is possible that this inequality, combined with the shift of the maxima, is the cause of the lack of resolution.

WITHERITE ($BaCO_3$).

(Massive, crystalline. Curve *b*, fig. 2.)

The reflection decreases normally from 4 to 6 μ followed by strong complex reflection band, with maxima at 6.78 and 6.98 μ. The latter band is the more intense, which is just the opposite of the carbonates, having a metal of less molecular weight. The specimen had an unusually high polish, which accounts, in part, for the high reflection maximum.

MALACHITE ($CuO \cdot CO_2 \cdot H_2O$).

(Concretionary specimen. From Burra Burra, South Australia. Curve *a*, fig. 3.)

The specimen of malachite was highly polished. The reflection bands are well resolved, while the second maximum is of the usual intensity for carbonates. Beyond 10 μ there appears to be another band, but the unsteadiness of the galvanometer prevented an accurate determination of this question. The maxima of malachite occur at 6.66 and 7.3 μ, with a possible third band at 7.8 μ.

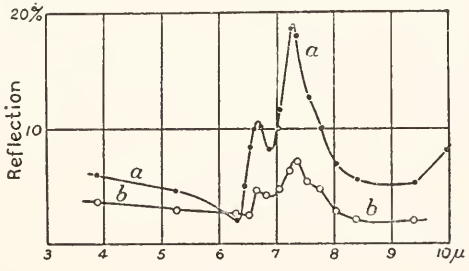

FIG. 3. — Malachite (*a*); Azurite.

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AZURITE ($3CuO \cdot 2CO_2H_2O$): CHRYSOCOLLA ($CuSiO_3 + H_2O$).

(From Lyon County, Nevada. Curve *b*, fig. 3.)

The specimen examined was a mixture of azurite and chrysocolla, the first mineral being present in only a small amount. No silicate bands at

8.5 and 9 μ could be detected. The reflecting power is low, which is no doubt due to the presence of the silicate. The maxima at 6.65, 7.3, and 7.8 μ are in common with those of malachite. The transmission curve of azurite is given in the preceding volume. It shows the OH band at 3 μ and the carbonate bands at 3.5 and 4 μ.

DOLOMITE [$CaMg(CO_3)_2$].

(A plane cleavage piece. From Traversella, Italy. Curve *a*, fig. 4.)

Dolomite is of interest because it is a double carbonate of Mg and Ca. The reflecting power is high. The first band is in common with that of

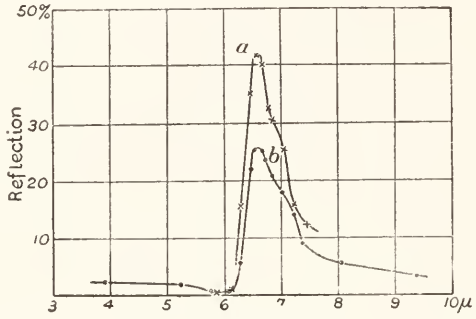

FIG. 4. — Dolomite (*a*); Siderite.

$CaCO_3$, while the second band is to be found in $MgCO_3$. The maxima occur at 6.58 and 6.95 μ.

SIDERITE ($FeCO_3$).

(Cleavage piece. From Allevard, France. Curve *b*, fig. 4.)

The reflection curve of siderite is composed of a complex maxima similar to that of dolomite. The maxima occur at 6.6 and 7.1 μ.

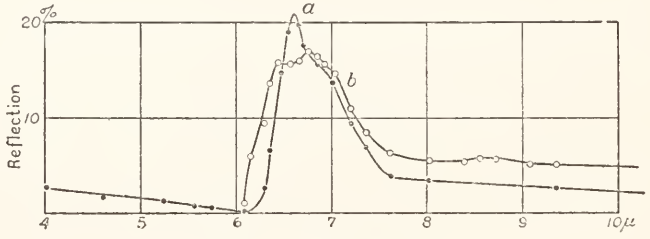

FIG. 5. — Calcite (*a*); Magnesite.

CALCITE ($CaCO_3$).

(Curve *a*, fig. 5.)

The reflection curve is obtained from a natural cleavage face of Iceland spar. The reflection band is complex with maxima at 6.6 and 6.85 μ. The reflection bands in the deep infra-red will be noticed presently. It is

desirable to examine aragonite, $CaCO_3$, which differs from calcite in its crystalline form, to determine the effect of structure; this is given in Chapter III. It was shown in Carnegie Publication No. 35 that isomeric compounds have different transmission spectra; and one would expect also the reflection spectra of isomers to be different. The unsteadiness of the galvanometer prevented the location of the band, found by Aschkinass, at 11.4 μ. In this region the radiometer would have been more satisfactory.

MAGNESITE ($MgCO_3$).

(Massive. Curve *b*, fig. 5.)

The sample examined was an opaque white mass which took a high polish. The band of selective reflection is very similar to that of calcite and consists of two maxima at 6.5 and 6.8 μ, respectively.

As a whole the carbonates are conspicuous for a double band of metallic reflection at 6.5 to 7 μ which previously had not been resolved in calcite. The shift of these bands with increase in molecular weight of the metallic ion will be discussed on a later page. That the shift is not due to a change in the adjustment of the apparatus was verified at the completion of the observations by examining several of the specimens in succession, when it was found that the maxima coincided with the values first observed.

SULPHIDES.

The reflection spectra of sulphur and of the sulphides of Zn, Sb, Fe, and Pb were described in the preceding volume. Sulphur and sphalerite (ZnS) have a low reflecting power of only about 8 per cent throughout the spectrum to 15 μ. The remaining minerals have a high reflecting power of 32 to 36 per cent throughout the spectrum to 15 μ, where the reflection of stibnite, Sb_2S_3, seemed to decrease. The present examination includes four new sulphides.

MOLYBDENITE (MoS).

(Massive foliated. From South Australia. Curve *a*, fig. 6.)

This mineral is very soft, like graphite. The specimens were folded and distorted so that it was not possible to grind a surface parallel to a cleavage plane. The surface took a high polish, but no luster as is found in the cleavage lamina. The reflection curve is fairly uniform beyond 4 μ, which would indicate that the lack of polish had no serious effect beyond this point. The reflecting power is low and uniform (18 to 20 per cent, as compared with stibnite, 35 per cent) throughout the spectrum to 14 μ, which is to be expected from its electrical conductivity. (For further references to electrical conductivity, etc., see Carnegie Publication No. 65, p. 93; also Königsberger, Jahrb. Radioaktivität & Elektronik, vol. 4, p. 161, 1907.)

PYRRHOTITE [(Fe, Ni)S].

(Massive. From Sudbury, Ontario. Curve *b*, fig. 6.)

The specimen examined did not appear so highly polished as molybdenite. It is composed of a bright metal and a darker background. The reflecting power is higher than that of MoS, and increases rapidly with wave-length through the spectrum of 14 μ.

CHALCOCITE (Cu_2S).

(Curve *c*, fig. 6.)

The reflecting power rises rapidly from 15 per cent at 1 μ to 45 per cent at 4 μ, while beyond 7 μ the reflecting power has a fairly constant

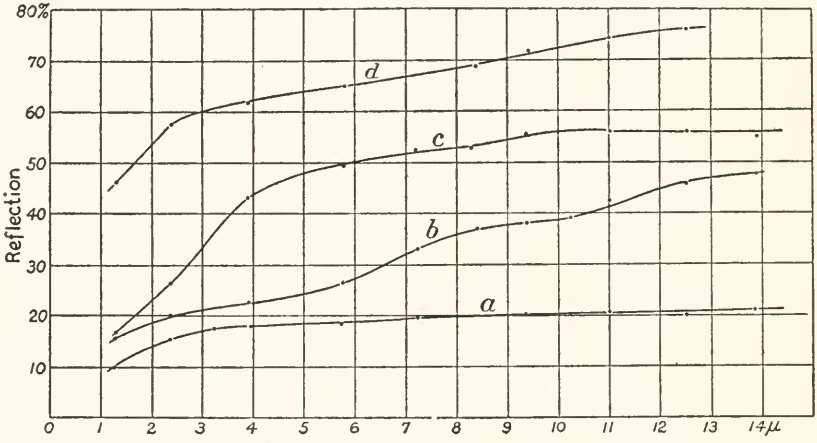

FIG. 6. — Molybdenite (*a*); Pyrrhotite (*b*); Chalcocite (*c*); Covellite.

value of 55 per cent. This substance is black, not unlike magnetite and the Siberian graphite previously described. The polish was higher than in pyrrhotite.

COVELLITE (CuS).

(From Anaconda Mine, Butte, Montana. Curve *d*, fig. 6.)

This mineral is of a steel-blue color, and appears as compact as steel. The reflecting power rises rapidly at 1 and 2 μ and then more slowly to 14 μ, where it amounts to 75 per cent.

As a whole, the examination of the sulphides shows that the sulphur atom has merely reduced the reflecting power of the metal, but has not brought about any bands of selective reflection in the region examined. In the case of sphalerite (ZnS) the sulphur atom has introduced into the metal a property which is to be found only in non-metals, viz, low reflecting power and selective absorption in the infra-red. Of the elements which are on the border line between metals and non-metals, selenium behaves like a metal in its high reflecting power (see fig. 7) and absence of infra-red absorption bands, while iodine and sulphur (non-metals) have absorption bands in this region.

SELENIUM (Se).

(Curve *d*, fig. 7.)

Selenium has practically the same reflecting power (18 to 20 per cent) as molybdenite. Pfund (Johns Hopkins Univ. Circular No. 4, 1907) has made a thorough investigation of the infra-red polarization of this substance.

OXIDES.

In the previous examination only quartz (SiO_2) represented this important group of minerals.

MAGNETITE (Fe_3O_4).

(From Port Henry, Essex County New York. Curve *a*, fig. 7.)

The surface examined was a triangular crystal, face about 3 cm. on an edge. The specimen was very homogeneous, but did not take a high polish, sufficient to observe the reflected image of an object at a small angle of incidence. The reflecting power rises uniformly throughout the spectrum, showing that the observations are affected by the lack of polish.

HEMATITE (Fe_2O_3).

(From Cumberland, England. Curve *b*, fig. 7.)

The specimen examined was a very dense homogeneous concretion, polished parallel to the radius of growth. The surface had a high polish (better than that of magnetite), reflecting a strong image of a source at a

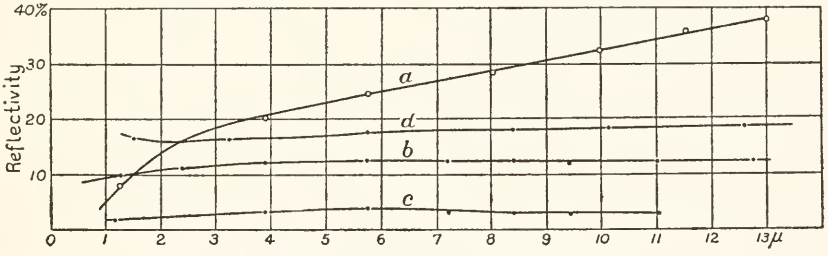

FIG. 7. — Magnetite (*a*); Hematite (*b*); Chromite (*c*); Selenium.

small angle of incidence. The reflecting power, in the infra-red, is far below that of magnetite, although it is higher in the visible. The reflecting power is uniformly 12 per cent, from which it would appear that this is the normal value for hematite.

CHROMITE (FeO, Cr_2O_3).

(From Lancaster County, Pennsylvania. Curve *c*, fig. 7.)

The surface of this dark specimen was mottled, parts of which took a high polish. The reflecting power is uniformly 4 per cent throughout the spectrum.

It is of interest to note that the iron oxides show no bands of selective reflection in the region of the spectrum up to 15 μ; zincite, ZnO, fig. 9, is another example.

SCHEELITE ($CaWO_4$).

(Massive. From Armidale, New South Wales. Curve *a*, fig. 8.)

The reflection power of this mineral behaves in the usual manner, being low in the region of the spectrum up to 11 μ, followed by a strong complex band of selective reflection, the maximum of which extends from 11.3 to 12.5 μ, the possible single maxima being at 11.3, 11.8, and 12.4 μ. The reflecting power is unusually low on the long wave-length side of the reflection band.

ZIRCON ($ZrSiO_4$).

(Near Eganville, Renfrew County, Ontario. Curve *b*, fig. 8.)

The specimen examined was a large rectangular cleavage piece, about 3 by 3 cm., of brownish color, semitransparent in thin sections.

Although this is a double oxide of zircon and silicon, the reflection curve is entirely different from the silicates previously studied. The strong band of selective reflection occurs farther toward the long wave-lengths, the single maxima (not well resolved) being at 10.1, 10.6, and 11 with a pos-

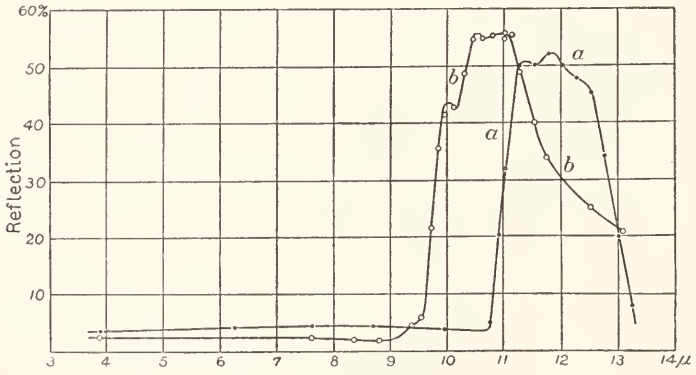

FIG. 8. — Scheelite (*a*); Zircon.

sible band at 11.7 μ. As a whole the reflection curve is exactly the same as that of willemite, Zn_2SiO_4, previously studied. In the latter, the bands are well resolved and occur at 10.1, 10.6, 11.0, and 11.6 μ. From this it would appear that in these two minerals the effect of SiO_2 is different from that found in quartz and in the minerals commonly known as silicates, viz, silicates of Ca, Mg, Fe, etc. Some of the latter, however, have the last band lying close to the first band in the present silicates.

WULFENITE ($PbMoO_4$).

(Red Cloud Mine, Yuma County, Arizona. Curve *a*, fig. 9.)

This is a chrome-red crystal. A natural crystal face, 1.5 by 2 cm., having a high polish, but not perfectly plane, was examined. In spite of this the reflection curve is one of the most remarkable yet found. The band of metallic reflection is almost as strong as quartz. There are two

maxima, at 11.75 and 13.1 μ, respectively. The reflecting power decreases uniformly from 12 per cent at 4 μ to 10 per cent at 8 μ, passes through a minimum of 4 per cent at 10.8 μ, then suddenly rises to 78 per cent at 11.75 μ.

RUTILE (TiO_2).

(Graves Mountain, Lincoln County, Georgia. Curve *b*, fig. 9.)

The surface of the specimen examined was a natural crystal face, area about 1.4 by 1.8 cm., having a high polish, but uneven and containing cracks.

The reflection curve is the most unusual of all examined in that the band of selective reflection occurs almost at the working limit of a rock-salt prism. The maximum is broad and is fairly well defined at 13.6 μ.

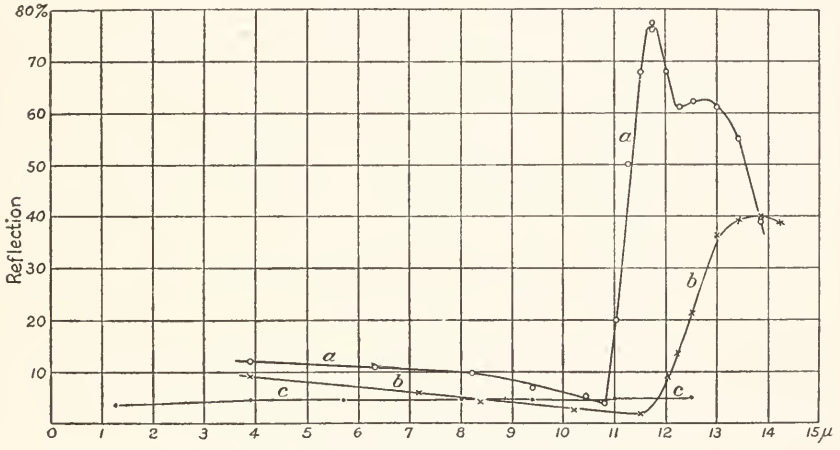

FIG. 9. — Wulfenite (*a*); Rutile (*b*); Zincite.

ZINCITE (ZnO).

(From Franklin, New Jersey. Curve *c*, fig. 9.)

The specimen examined was massive, having a red color and a dull polish. The surface was full of cracks, which would materially reduce the reflecting power. The reflecting power is low and uniform throughout the region of the spectrum examined. No bands of selective reflection were found. In this respect zincite is similar to iron oxide, but, on account of its low reflecting power, it is to be classed with the "insulators," and hence one would expect to find bands of selective reflection in the infra-red.

CORUNDUM (Al_2O_3).

(Craigmont, Renfrew County, Ontario. Curve *b*, fig. 10.)

This specimen was an opaque crystal, of which a cleavage surface, about 2 by 3 cm. in area, was examined. The surface contained striæ, but otherwise had a high polish. The reflecting power is unusually low, except in the region of selective reflection, when it is quite high. The region of selective reflection is wide with maxima at 11.0, 11.8, and 13.5 μ.

ALUMINUM SILICATES.

There is no special reason for thus classifying the following minerals, except that most of them are quite unlike the commoner silicates previously examined.

Cyanite ($Al_2O_3SiO_2$).

(Yancy County, North Carolina. Curve *a*, fig. 10.)

The color of this flat crystal was light green. The flat crystal face, 2.5 by 3.5 cm., was ground but did not have a high polish. The band of selective reflection has three sharp maxima, at 9.3, 9.78, and 10.28 μ,

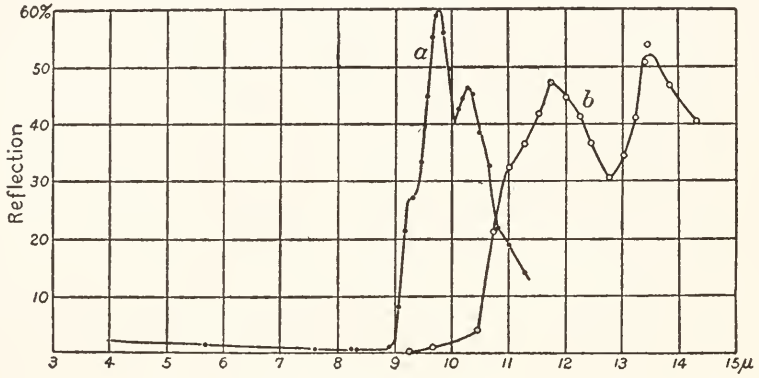

Fig. 10. — Cyanite (*a*); Corundum.

respectively, and is not unlike that of willemite (Zn_2SiO_4), except that in the latter the whole band is shifted to longer wave-lengths with the maxima at 10.1, 10.6, and 11 μ.

Beryl [$Be_3Al_2(SiO_3)_6$].

(From North Carolina. Fig. 11.)

The surface examined was ground on a crystal face. The specimen was opaque and green in color. The reflection curve follows the usual course with a band of selective reflection extending from 8 to 10.5 μ. The

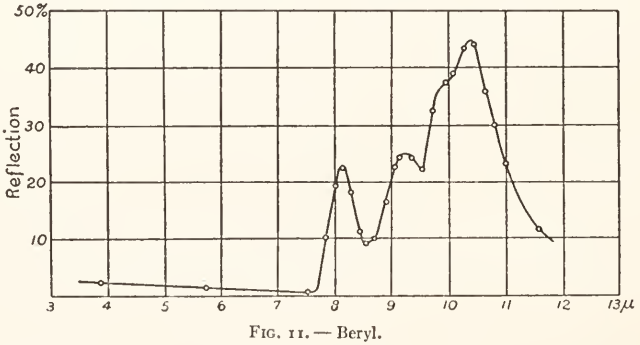

Fig. 11. — Beryl.

maxima are not so high as usual with silicates, but they are sharp and occur at 8.15, 9.2, 9.9, and 10.4 μ.

TOPAZ [$(Al, F)_2SiO_4$].

(Villa Rica Mines, Geraes, Brazil. Curves *a* and *b*, fig. 12.)

The specimen from Brazil was a yellow rectangular prism with faces 1 by 2.5 cm. The natural face, which had a high polish, was examined. The reflection curve *a*, fig. 11, is low throughout the spectrum, except in

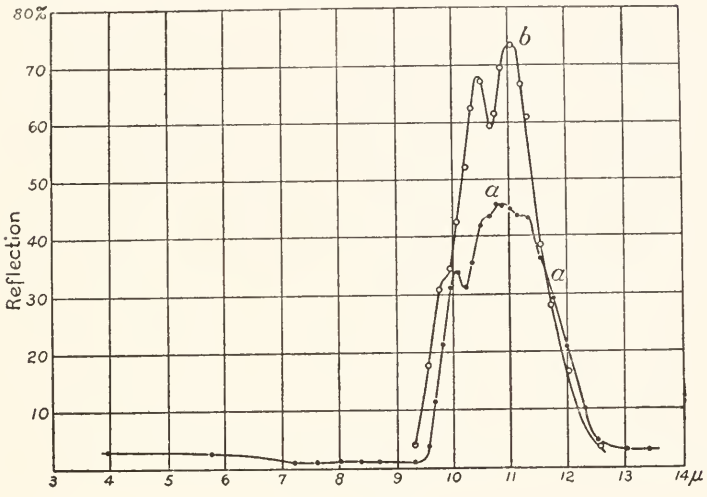

FIG. 12. — Topaz.

the region of selective reflection, which extends from 10 to 11.5 μ with unresolved maxima at 10.05, 10.6, 10.9, and 11.3 μ.

The white topaz examined, curve *b*, fig. 11 (in its highest part), is an almost exact reproduction of the quartz curve, with the exception that the latter is shifted to the longer wave-lengths. The white topaz, which was ground and had a fairly high polish, has sharp maxima at 9.9, 10.45, and 11 μ with a possible band at 12 μ. The band at 11 μ is in common with that of several other silicates.

SODIUM SILICATE (Na_2SiO_3).

(Curve *b*, fig. 13.)

The curve of liquid glass is similar to that of the glasses previously examined. This is one of the simplest obtainable chemical compounds of the silicates, and is further evidence that the silicon oxide radical is not so constant in its behavior toward heat-waves as was found in the CO_2 radical of the carbonates.

SPODUMENE [$LiAl(SiO_3)_2$].

(From Pennington County, South Dakota. Curve *a*, fig. 13.)

This mineral is of the same composition as kuntzite, the transmission curve of which is given on a later page. The specimen examined was a polished cleavage piece from a large gray crystal. The maxima of the selective reflection bands occur at 9.18, 9.7, and 10.4 μ, respectively.

In conclusion, it may be said that, from all of the silicates examined, there is no regularity in the position of the maxima such as obtains in the sulphates and the carbonates. It is true that in a few cases the maxima are in common, but, on the whole, the evidence indicates that there is no uniform group of atoms acting in common as is found in the sulphates and carbonates. In other words, the silicon radical is different in the

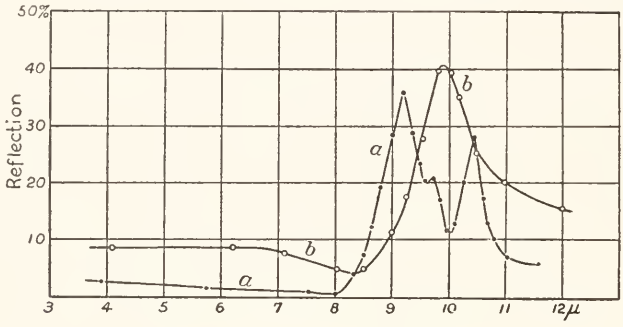

FIG. 13. — Spodumene (*a*); Sodium silicate.

different minerals. This seems to be the necessary interpretation to be given, for it has been impossible to work out a relation with the molecular weight of the molecule, such as exists in the carbonates and sulphates, to be discussed on a later page.

CHAPTER III.

MINUTE EXAMINATION OF THE REFLECTION BANDS OF QUARTZ AND OF THE CARBONATES.

Having assembled a fluorite prism and bolometer for radiation work, it seemed worth while to spend some time on the examination of the reflection bands at 6 to 7 μ in the carbonates, and at 8.5 to 9 μ in quartz. The fluorite prism had a circular aperture of 3.3 cm., angle 60°, and was perfectly clear. It was mounted on the spectrometer used in the previous work and, for the regions of the spectrum examined, the dispersion was from 4 to 6 times that of rock salt. On account of the large dispersion and the small prism face, the deflections were only about one-tenth that previously used. The glower of the Nernst lamp was used in order to obtain a sufficiently strong source of radiation. The main objection in using a glower is its narrowness, which requires greater care in maintaining a constant adjustment. The bolometer strip was about 0.5 mm. or 4′ of arc, while the temperature sensibility was 1 mm. $= 5^{\circ} \times 10^{-5}$C. A radiometer would have been more satisfactory, but the bolometer was conveniently at hand. With this greater dispersion it was found that the reflection bands of some of the carbonates are quite complex, while in others there is but one band.

Quartz.[1]

(Crystal cut perpendicular to optic axis. Curve *b*, perfectly clear specimen of quartz glass, fig. 14.)

It has repeatedly been noticed that the various silicates have quite different reflection spectra, while in the carbonates and in the sulphates the spectra show great similarity. It was therefore assumed that the silicon oxide radical is differently united in the different silicates. All the evidence obtainable, without exception, of substances in the solid or liquid (crystalline or amorphous) condition, shows that crystallographic form does not explain these anomalies; neither will the slight impurities present in many of the silicates explain them.

Pfund [2] found identical reflection bands of sodium-potassium tartrate ($C_8H_4K\ NaO_6+4H_2O$) in the form of a polished crystal, and also in the molten condition. His reflection maxima of molten nitroso-dimethylani-

[1] The writer is indebted to Dr. Day and Mr. Sheppard, of the Geophysical Laboratory of the Carnegie Institution of Washington, for the sample of quartz glass.

[2] Pfund, Astrophys. Jour., **24**, p. 31, 1906.

line [$(CH_3)_2NC_6H_4NO$] coincide with the absorption maxima found by the writer for a solid film of this compound. Furthermore, the writer found that reflection spectra of solids in solution may or may not be identical with that of the solid, noteworthy examples being the sulphates of copper and of sodium. The cause of the reflection bands is therefore to be sought within the molecule.

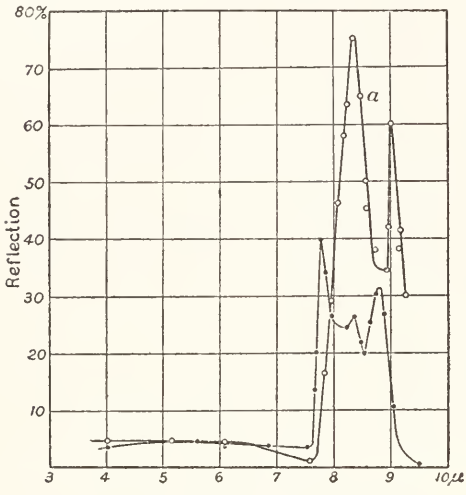

Fig. 14. — Quartz: (*a*) Crystalline; (*b*) Amorphous.

From the fact that the physical and chemical properties of quartz-glass are different from the crystal, one would infer that there is a difference in the molecular structure. This is well illustrated in fig. 14. The reflection spectrum of the amorphous material is entirely different from that of the crystal. It seems to have no connection with any of the silicates examined. The maxima of the reflection spectrum of crystalline quartz occur at 8.4 and 9.02 μ, while those of the amorphous quartz are found at 7.8, 8.4, and 8.8 μ, respectively. The intensity of the maxima of bands of the amorphous quartz is not so great, neither does the reflecting power, in the region of the spectrum just preceding a reflection band, fall to so low a value as in crystalline quartz.

In this connection it may be noticed that the various kinds of glass (sodium silicates) previously examined have similar reflection spectra.

Calcite and Aragonite ($CaCO_3$).

(Fig. 15. Curve *a*, calcite; curve *b*, aragonite.)

From the fact that, although the carbonates examined belong to only two crystal systems,[1] the reflection spectra are different, one would infer that the cause is not to be attributed to crystalline form. Previous examinations have shown that isomeric substances have different spectra. One would therefore expect to find the spectra of calcite and aragonite to be different, as was previously found for orthoclase and microclene ($KAlSi_3O_8$) at 8 to 10 μ. The fact that the substances are inorganic, and that the reflection bands are far in the infra-red, is of interest but non-essential.

In fig. 15, curve *a* gives the reflection from the plane, highly polished

[1] To the *rhombohedral* system belong $CaCO_3$ (calcite), $MgCO_3$, $FeCO_3$, and $ZnCO_3$; to the *orthorhombic* system belong $CaCO_3$ (aragonite), $BaCO_3$, $SrCO_3$, and $PbCO_3$. In the former group the band toward the shorter wave-length appears to be the most intense, while in the latter group the bands seem sharper and of more uniform intensity.

cleavage face of Iceland spar. With the larger dispersion the band previously found at 6.6 μ is now resolved into two bands with maxima at 6.5 and 6.6 μ, respectively. The region at 7 μ is evidently still more complex, but not resolved even with this greater dispersion. In curve *b* is given the reflection spectrum of a clear crystal of aragonite. The crystal face was small, only about 6 by 15 mm., and since the area of the comparison mirror was not reduced in like proportion, the reflecting power of the maxima is really higher than here given. In fact, for a well-polished crystal the reflecting power is no doubt as high as for calcite. The important point of interest in the present examination is that aragonite has only two reflection maxima, of about equal intensity, and located at 6.53 and 6.75 μ, respectively.

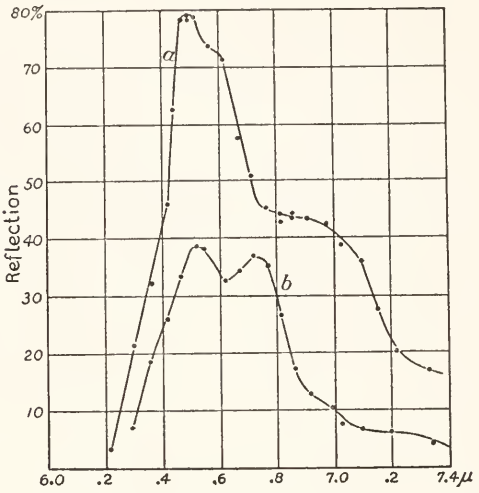

FIG. 15. — Calcite (*a*); Aragonite.

MAGNESITE ($MgCO_3$).

(Curve *a*, fig. 16.)

This sample was previously examined (fig. 5). In the present curve there are three bands with maxima at 6.42, 6.65, and 6.9 μ.

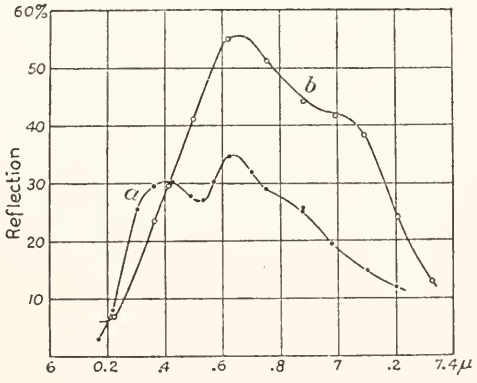

FIG. 16. — Magnesite (*a*); Smithsonite.

SMITHSONITE ($ZnCO_3$).

(Curve *b*, fig. 16.)

This sample was previously examined (fig. 1), when two maxima were found. In the present examination the bands are more resolved, but the maxima occur at 6.65 and 7.05 μ, respectively, as in the previous investigation.

STRONTIANITE ($SrCO_3$).

(Curve *a*, fig. 17.)

The band at 6.68 μ is not resolved even with the large dispersion of fluorite. The band is symmetrical, as previously found in fig. 2.

WITHERITE ($BaCO_3$).

(Curve *b*, fig. 17.)

The pair of bands is somewhat better resolved, with maxima at 6.7 and 6.97 μ, respectively, the same as was found in the previous examination of this same specimen (see fig. 2). The reflecting power is slightly lower

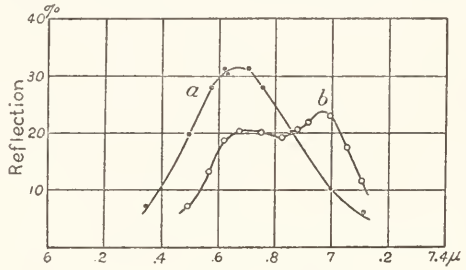

FIG. 17. — Strontianite (*a*); Witherite.

but that is to be attributed to the difference in the adjustment, *i.e.*, the faces of the comparison mirror and of the substance may not have been in the same plane. As a result they would not reflect the same part of the image of the glower upon the spectrometer slit. This is of minor importance since we are not concerned with the absolute reflecting power.

On a subsequent page it is shown that an emission band of Adularia occurring at 2.9 μ is shifted to 3.2 μ in the absorption spectrum of the crystalline material. Using polarized energy, the reflection bands of the carbonates depend upon the direction of vibration of the incident energy. The author therefore hopes to investigate water solutions to learn the behavior of these reflection bands, using polarized radiation.

CHAPTER IV.

REFLECTION SPECTRA IN THE EXTREME INFRA-RED.

From the foregoing work on selective reflection in which a single reflecting surface was used, it is apparent that by successive reflection of heat-waves from several surfaces there will remain only the residual rays lying in the region of selective reflection. It was noticed that the reflecting power in the region of 4 to 8 μ is only about $\frac{1}{10}$ that of the band of selective reflection. Hence, after reflecting from three surfaces the intensity would be only $\frac{1}{1000}$, and after five reflections only $\frac{1}{100000}$.

Rubens and Nichols [1] were the first to apply this method in locating the maxima of the residual rays of a series of substances including quartz, mica, fluorite, rock-salt, sylvite, crown and flint glass, sulphur, alum, and calcite. By using a grating of fine wire they were able to extend their observations to 61 μ, the longest heat-waves yet identified. Of the above-mentioned substances, only the first four were found to have bands of residual rays in the extreme infra-red.

Aschkinass [2] did some further work on this subject, examining marble, calcite, selenite, alum, sodium bromide, and potassium bromide. He found a band of residual rays at 29.4 μ in marble, and showed that similar bands exist in the bromides, the maxima of which lie beyond 60 μ.

From the results obtained with the silicates (see Carnegie Publication No. 65, pp. 80 to 90), especially glass, it becomes apparent that one can hardly expect to locate bands of residual rays in the extreme infra-red, even at 18 to 20 μ, unless they are much more intense than those found in the region of 8 to 10 μ. For it is necessary to have several reflecting surfaces to eliminate the large amount of energy of short wave-lengths as compared with the small amount to be measured, of the long wave-lengths. As is well known now, in the case of quartz, rock-salt, and sylvite, this is an easy matter on account of the high reflecting power of these bands. For example, for the band at 61 μ, which was examined after reflection from five surfaces of sylvite, it was found that the reflecting power of sylvite is 80 per cent. The galvanometer deflections were only about 5 mm. in the maximum of the band. If the reflecting power were only one-half this amount (*cf.* the silicates), the galvanometer deflection after five reflections would be one thirty-second of 5 mm., which could not be

[1] Rubens and Nichols, Ann. der Phys. (3), 60, p. 418, 1897.

[2] Aschkinass, Ann. der Phys. (4), 1, p. 42, 1900.

observed with accuracy. In the case of the silicates (as compared with quartz), where the height of the reflection band at 8 to 10 μ is always considerably less than 50 per cent, after three reflections the galvanometer deflections would be only 1 or 2 mm. at 18 to 20 μ. It does not follow, therefore, because no residual rays of a substance are to be found in the region of 18 to 20 μ, as was the case in the present examination, that no bands exist, but that they are too weak to be measured. From the similarity of the spectra, throughout the infra-red, of great groups of chemically related compounds, and from the fact that quartz and mica have bands of residual rays in the region of 18 to 20 μ, it is to be assumed that the silicates, in general, are selectively reflecting in this region. The fact that no bands were found is to be attributed to the weakness of the reflection bands.

As a whole, however, the reflecting power of some of these bands is very high. One has really no conception of the state of affairs until he examines a substance like quartz. The phenomenon is so easily observed with quartz that it might well serve as a general laboratory experiment. In regard to the ease of observing in the infra-red, the writer's experience has extended from the optical region into the most remote infra-red, and it may be said that more difficulty was experienced in the region of 12 to 15 μ, on account of the absorption of the rock-salt prism, than in the region of greater wave-lengths. The actual intensity in the emission spectrum differs greatly throughout the spectrum. For example, Rubens and Aschkinass (*loc. cit.*) compute that for a temperature of 2000° the maximum emission at 1.5 μ is 800,000 times as great as at 60 μ.

APPARATUS AND METHODS.

In the present examination the usual methods of procedure were employed. The spectrometer was the one used in previous work. The spectrum was produced by means of a wire grating *G*, fig. 18. The grating was made by the well-known method of winding two copper wires of the same diameter on a brass frame. One wire was then unwound and the remaining one was fastened to the frame by means of an electrolytic deposit of copper. The strands were then cut from one side of the frame. The wire was not of uniform thickness, so that the grating was far from perfect. Such a grating has the well-known property of producing only the odd order of spectra. On account of its imperfections it was not possible to make accurate measurements on orders higher than the seventh, using a Bunsen sodium flame. Two gratings were employed, the one (No. 2) having a constant of $K=0.2120$ mm., for the other $k=0.3279$ mm., determined with the sodium flame. The coarser grating was the more uniform in its individual windings, but in one region the wires were more closely but very regularly wound. The magnesite band at 29.4 μ was apparently double, at least very wide, just as though this grating spectrum

contained "ghosts." For the main part of the investigation grating No. 2 was used, which on account of the finer wires was not so regular in its winding. Using three reflections from quartz it was possible to observe the third order maximum of the band of wave-length, 9.05 μ; in all other cases, the third order spectrum was too weak for observation. A grating having wires of more uniform diameter and more uniformly wound, *e.g.*, wound on a screw thread, would no doubt have been more efficient in producing a pure spectrum.

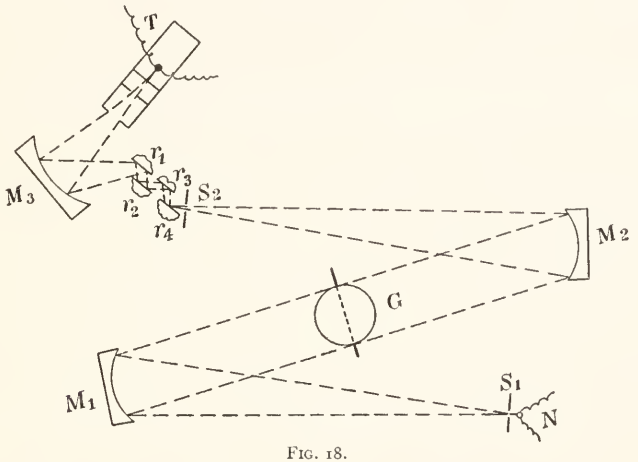

FIG. 18.

The spectrometer arm carrying the Nernst "heater," the slit S_1 and the mirror, m_1, was movable. The plane of the grating was made normal to the beam of light by placing a mirror on the wires and revolving the grating until an image of the slit, S_1, was projected back upon the slit. It was not convenient to have the collimating mirror and the grating revolve about the spectrometer axis, which is necessary to maintain the same grating constant. Accordingly the grating was kept in a fixed position and the spectrometer arm, carrying the mirror and source, was revolved about it.

The apparatus was calibrated by locating the maxima of the selective reflection bands of substances previously examined by Rubens and Nichols and by Aschkinass, viz, quartz at 8.7 and 20.75 μ, mica at 18.4 and 21.25 μ, fluorite at 24.4 μ, and calcite at 29.4 μ. The calibration curves are shown in fig. 19, where curve *a* is for the grating having a constant $K=0.3279$ mm. (for Na), and curve *b* is for the grating (No. 2) having a constant $K=0.2120$ mm. (for Na). In this curve the abscissæ are the maxima of reflection bands and the ordinates are the rotations of the spectrometer arm from the zero position. Blocks of wood with vertical metal plates, having openings 2 by 3 to 4 by 5 cm. were mounted securely upon a board, as shown at r_1, r_2, r_3, r_4. The minerals were secured to the back of the metal

plates by means of soft wax, the plane faces being, of course, placed over the openings in the plates. In case less than four reflecting surfaces were available, aluminum mirrors were placed in the remaining holders. A short focus mirror projected an image of the slit, S_2, upon an improved iron-constantan thermopile of 20 junctions. The wire used in the thermopile was only 0.075 mm. in diameter. This eliminated heat conduction and there was no drift of the zero. The galvanometer suspension weighed about 10 mg., which eliminated the effect of earth tremors. This, however, necessitated lengthening the period to gain great sensitiveness. The

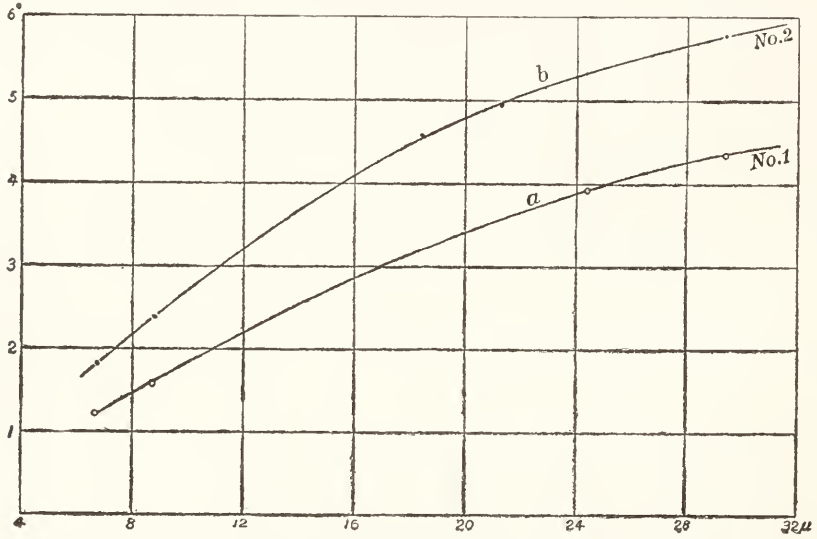

FIG. 19. — Wire-grating calibration.

thermopile was in a metal case, wrapped in felt, and the complete outfit was perfectly steady. It was, therefore, possible to increase the period of the galvanometer to 20 to 30 seconds (single swing) when its sensitiveness was $i = 5 \times 10^{-11}$ ampere on a scale at 1 m. The resistance of the thermopile was 8.9 ohms. The galvanometer resistance was 5 ohms, from which it was computed that a deflection of 1 mm. $= 7 \times 10^{-7}$ °C. for a scale at 1 m.

From this it will be seen that the temperature sensitiveness of the instrument was as great as, and in some instances greater than, in previous investigations. Hence, it appears that in numerous cases the absence of reflection bands is to be attributed to some property in the material rather than to a fault in the instruments.

The whole apparatus was, of course, thoroughly protected from stray light by providing numerous black pasteboard screens.

RESIDUAL RAYS[1] FROM MICA.

Muscovite Mica [$H_2KAl(SiO_4)_3$].

In fig. 20 are plotted the spectrometer arm rotations (abscissæ) and the galvanometer deflections in the grating spectrum of mica. The sharp maximum at A is the central image, while B_1 is the selective reflection band (first-order spectrum) in the region of 9 μ. For this part of the curve three reflection surfaces were used, while to obtain the part C_1, C_2 four reflecting surfaces were employed. The latter bands are plotted to a larger scale in C'_1 and C'_2. The maxima in the spectrum to the left (not

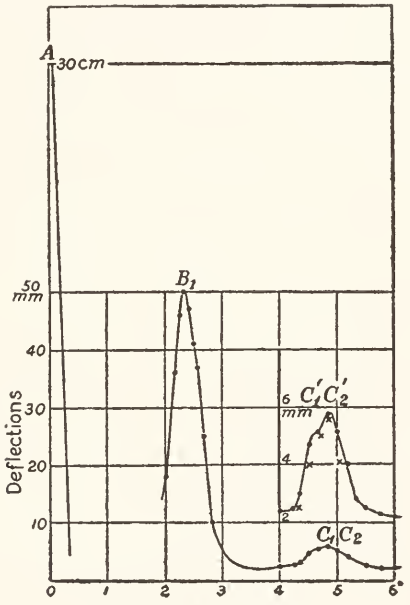

Fig. 20. — Muscovite mica.

plotted) were identical with the above. The wave-lengths of the maxima at C_1, C_2 are 18.4 and 21.25 μ (Rubens and Nichols) and are used in the calibration curve of grating No. 2, curve *b*, fig. 19.

RESIDUAL RAYS FROM CARBONATES.

Calcite ($CaCO_3$).

(Grating No. 2. K = 0.2120 mm. Fig. 21.)

The plane cleavage faces of 3 large crystals were used in this examination. The spectrometer slits were 4 mm. wide. In fig. 21 the central

[1] It is a pleasure to note the general adoption of the expression " residual rays " for the meaningless " reststrahlen," formerly used. The English vocabulary seems sufficiently complete to enable writers to find equivalents to " étalon," " entladungsstrahlen," etc.

image A is plotted to one-fifth the scale of B_1 and B_2, while the scale of C'_1, C'_2 and D'_1, D'_2 is five times that of B_1, B_2. The sharp maxima at B_1 B_2 are due to the complex reflection band at 6.7 μ, previously studied. In the present case the maximum occurs at 1°49′, which corresponds to 6.78 μ. The wave-length of the maximum at 5° 45′, D_1, D_2 is 29.4 μ as determined by Aschkinass (*loc. cit.*). He located the maximum at C_1, C_2 at 11.4 μ in the rock-salt spectrum, but did not find it in the grating spectrum. From his observations he predicted a weak band in the region of 15 to 20 μ. The asymmetrical part of the reflection curve at +4° indicates a possible band at 14 to 16 μ, beginning also in the transmission curve

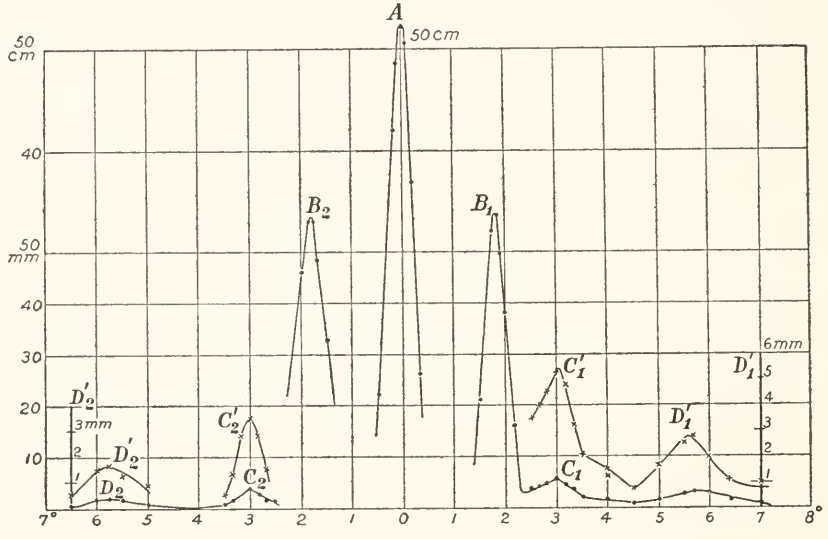

Fig. 21. — Calcite.

of calcite, previously studied (see Carnegie Publication No. 65, p. 70), where the substance becomes entirely opaque at 14 μ.

The band at 11.4 μ deserves further study because of the possibility of its being dependent upon the direction of polarization of the incident energy.[1] In the transmission curve of calcite previously studied (see Carnegie Publication No. 65, p. 70) it was found that the region of 9 to 14 μ is quite transparent. A small absorption band was found at 11.3 μ, which is so inconspicuous that it would appear impossible for it to give rise to selective reflection. Of all the substances examined this is the first example (see, however, nitrosodimethyl aniline) where a *small* absorption band apparently coincides with, or gives rise to, a reflecting band. In all other

[1] While this paper is in press, Nyswander (Phys. Rev., **26**, p. 539, 1908), using polarized light, found that the band at 11.3 μ is due to the complete absorption (reflection) of the extraordinary ray, the ordinary ray showing no trace of an absorption band in this region. At 14.1 μ is a band due almost entirely to the complete absorption of the ordinary ray.

cases the transmission curves show complete opacity in the region of a selective reflection band even for the thinnest film yet examined, viz, glass (see Carnegie Publication No. 65, p. 65). That the band at 29.4 μ is not influenced by the structure of the crystal is proven by the fact that Aschkinass found this band in white marble.

Magnesite ($MgCO_3$).

(Grating No. 2, fig. 22.)

In this examination three reflecting surfaces of the massive material were used, one of which did not have a high polish. The maxima at B_1, C_1, D_1 correspond to wave-lengths 6.7, 11.3, and 30.7 μ (5° 52′), respectively. In fig. 22 the maxima C'_1, C'_2 (=11.3 μ) and D'_1, D'_2 (=30.7 μ) are drawn to ten times the scale of B_1, B_2. The band at D_1 is

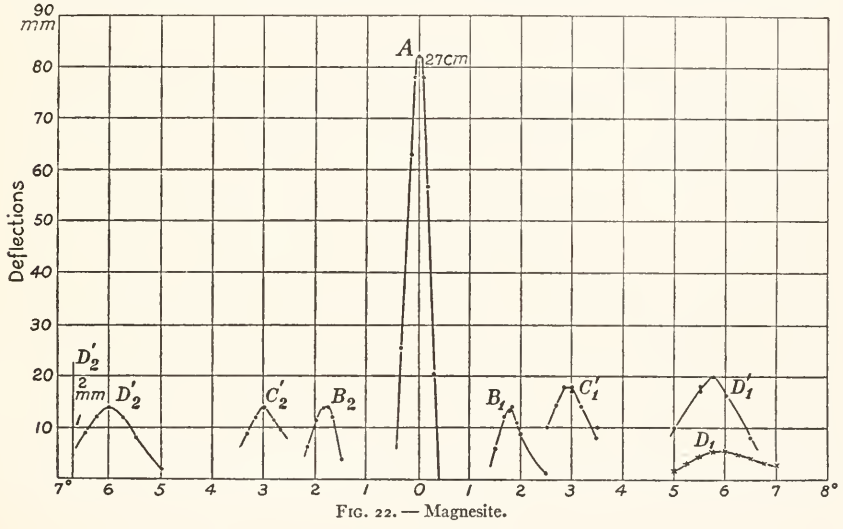

Fig. 22. — Magnesite.

plotted to the same scale as B_1 but only two reflecting surfaces were used. The magnesite maxima are identical with those of calcite (except at a possible greater wave-length, at 30 μ). This would seem to indicate that coincidence of the reflection spectra of chemically related groups of substances is a property which obtains throughout the spectrum. This is to be expected, but it seemed of interest to add further experimental evidence to support this view, by extending the observations into the remote infrared. The bands at 29.4 μ are too weak to illustrate the effect of molecular weight, noticed at 6.7 to 7.2 μ in the carbonates.

Residual Rays from Cryolite ($3NaF{\cdot}AlF_3$).

(Gratings No. 1; slits 4 mm.; fig. 23.)

Reasoning from the fact that cryolite is a fluoride of Na and Al, and from the behavior of fluorite (CaF_2), it was hoped to find this mineral to

have properties similar to fluorite. That the expectations were not fulfilled is perhaps to be attributed to the fact that the specimen was an hydrated alteration product, as will be noticed from its transmission spectrum (fig. 26), which shows that the mineral contained water.

In fig. 23 is given the reflection curve of cryolite, four large, well-polished surfaces being used. The central image was quite strong. The first-order

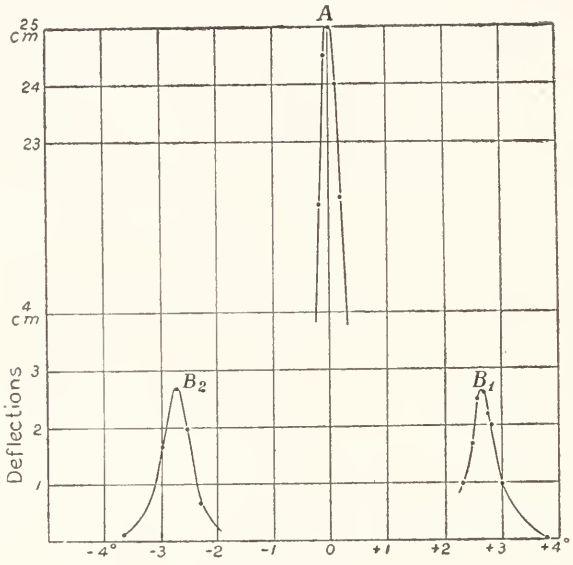

FIG. 23. — Cryolite.

diffraction band to the right and to the left is quite strong, being measured in centimeters instead of millimeters. This, of course, is partly due to the coarser grating. The mean angular position of the maximum is 2° 43′. From the calibration curve the wave-length of this maximum is 15.1 μ, which is just half the value of the most intense band of fluorite.

RESIDUAL RAYS FROM OTHER MINERALS.

DIASPORE [AlO(OH)].

In examining the following minerals grating No. 1 was used in order to obtain an intense spectrum. The slits were 4 mm., which is a little smaller than those used by others. In Carnegie Publication No. 65 the reflection spectrum of an intense double band was found at 14 to 15 μ. From its general trend it was hoped to find the reflection spectrum to contain further bands. Only two reflecting surfaces were available. With these, the maxima at 15 μ in the rock-salt spectrum were verified, but no bands were detected beyond this point.

STIBNITE (Sb_2S_3).

Stibnite was previously found to have a high reflecting power up to 15 μ, where it seemed to decrease. In the present examination, using three reflecting surfaces, this high reflecting power was found to continue throughout the infra-red. A small maximum was found at 2 μ, which no doubt belonged to the third-order diffraction band. When using aluminum mirrors a similar band was found at this point.

SPODUMENE [$LiAl(SiO_3)_2$].

Three large reflecting surfaces were used. The galvanometer was perfectly steady, so that 0.2 mm. deflections could have been read, but no radiation was detected beyond that due to the reflection bands at 9 to 10 μ previously examined with the rock-salt prism.

CELESTITE ($SrSO_4$). SELENITE ($CaSO_4+2H_2O$).

Three large cleavage specimens of each of these were examined, using slits 4 mm. wide. In the case of celestite the central image gave a deflection of 50+cm., but nowhere could radiation be detected except in the region of 9 to 10 μ previously studied. Aschkinass (*loc. cit.*) has predicted a band in the region of 50 μ for the sulphates.

APATITE [$Ca_5F(PO_4)_3$].

Three large ground and polished surfaces were used in this examination. No reflection bands were observed except at 9 μ, where an examination with a rock-salt prism showed a weak (20 per cent) double band. Apparently the phosphates have no strong reflection bands throughout the infra-red spectrum. This is just the opposite of what has been described in Chapter II on the oxides, where very intense bands were frequently observed.

CYANINE ($C_{29}H_{35}N_2I$).

(Grating No. 2; slits 4 mm.)

This substance was melted between glass plates, which were then split apart, thus leaving plane smooth surfaces. Three such films on glass were examined. It was previously found (see Carnegie Publication No. 35, p. 82) that cyanine is very opaque at 6 to 8 μ. The central image gave a deflection of 50+cm., and there was still a little reflected energy to be detected at 25 μ, indicating a high reflecting power, but no reflection bands could be detected throughout the spectrum.

SILICATES.

The reflection curve of mica has already been described in connection with the calibration of the instrument. This examination included also serpentine, albite, and microcline. The grating spectrum showed the reflection bands at 9 μ, but beyond this no appreciable radiation could be detected. This, of course, was to be expected for serpentine, for which

the rock-salt prism showed only weak maxima at 8 to 10 μ. In a previous study of quartz with a rock-salt prism a narrow, quite intense band was located at 12.5 μ, which had not been recorded by Rubens and Nichols. In the present examination, using grating No. 1, the maximum was found at 2° 21′ (= 12.8 μ), while with grating No. 2 the maximum was located at 3° 20′ (= 12.5 μ). In table I are given the maxima of the reflection bands of the minerals studied.

TABLE I. — MAXIMA OF REFLECTION BANDS.

	μ	μ	μ	μ	μ	μ	μ
Smithsonite, $ZnCO_3$	6.65	7.05					
Cerussite, $PbCO_3$	6.9	7.25					
Strontianite, $SrCO_3$	6.68						
Witherite, $BaCO_3$	6.70	6.98					
Malachite, $CuO \cdot CO_2 \cdot H_2O$	6.66	7.3	7.8?				
Azurite, $3\,CuO \cdot 2\,CO_2 \cdot H_2O$	6.65	7.32	7.8				
Dolomite, $CaMg(CO_3)_2$	6.58	6.95					
Siderite, $FeCO_3$	6.6	7.1					
Calcite, $CaCO_3$	6.4?	6.5	6.62	6.85 to 7.0	11.4	16.?	29.4
Aragonite, $CaCO_3$	6.53	6.75	7.0?				
Magnesite, $MgCO_3$	6.42	6.65	6.9	11.4	30.2		
Scheelite, $CaWO_4$	11.3 to 12.5	11.3 to 12.4					
Zircon, $ZrSiO_4$	10.1	10.6	11.0	11.6			
Wulfenite, $PbMoO_4$	3.2	6.5	11.75	13.1			
Rutile, TiO_2	13.6						
Cyanite, $Al_2O_3 \cdot SiO_2$	9.3	9.78	10.28				
Corundum, Al_2O_3	11.0	11.8	13.5				
Topaz $(Al \cdot F)_2SiO_4$:							
Yellow	10.05	10.6	10.9	11.3			
White	9.9	10.45	11.0	12.?			
Spodumene, $LiAl(SiO_3)_2$	9.18	9.7	10.4				
Muscovite Mica, $H_2KAl_3(SiO_4)_3$	9.2	9.7	10.2	18.4	21.25		
Cryolite, $3\,NaF \cdot AlF_3$	3.0	4.7	6.0	15.1			
Beryl, $Be_3Al_2(SiO_3)_6$	8.15	9.2	9.9	10.4			
Quartz:							
Glass	7.8	8.4	8.8				
Crystalline	8.4	9.02					

CHAPTER V.

ON REGULAR AND DIFFUSE REFLECTION.

From his previous work on the reflecting power of silicates the writer concluded that a surface like the earth or the moon, which is composed of silicates, must be selectively reflecting. From an examination of some of the subsequent discussions of the reflecting power of the moon, it would appear that a matte surface can not be selectively reflecting. In fact, the whole misunderstanding seems to hinge on this point. Since the surfaces of the minerals examined by the writer were, in nearly all cases, plane and highly polished, there was no "diffuse reflection," which is an entirely different question from the one of low, "practically zero," reflection, which the writer found to be a common property of certain minerals, for certain regions of the infra-red spectrum.

When energy is reflected from a plane smooth surface, it is commonly called "regular" (or, less accurately, "specular") reflection. On the other hand, energy reflected from a rough surface suffers "diffuse" reflection. The rough surface is equivalent to numerous small, plane, reflecting surfaces, the planes of which lie in all directions. In "diffuse reflection" for each infinitesimal surface, the ordinary laws of reflection are obeyed in full, unless the linear dimensions of the reflecting surface or of the rugosities or inequalities on it are small compared with the wave-length. However, the unpolished surface as a whole destroys all phase relation between the particles in the reflected wave-front, which is no longer plane, but irregular. (See Wood's Optics, p. 36.) This irregularity decreases as the angle of incidence increases, so that for a given roughness we get regular reflection. The long waves will be reflected first, then the shorter ones. "Smoked glass, which at perpendicular incidence will show no image of a lamp at all, will at nearly grazing incidence give an image of surprising distinctness, which is at first reddish, becoming white as the angle increases." (Wood's Optics, p. 37.)

The amount of energy reflected "regularly" from a plane surface will depend upon the reflecting power of the substance. Now, the reflecting power R of any substance is related to its index of refraction n and its absorption coefficient k by the equation

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}$$

For "transparent media," *i. e.*, "electrical non-conductors" (see

Drude's, also Schuster's Optics), the absorption coefficient is so low that it is negligible, and the reflecting power is a function of only the refractive index. Here the reflecting power is low, only 4 to 6 per cent, and decreases with increase in wave-length. All transparent media thus far examined (except silver chloride) have bands of selective reflection. In these bands the absorption coefficient k attains high values.

If k becomes sufficiently large (see Schuster's Optics, Pockel's Crystallographie, 1906), of the order unity, the absorption affects the reflecting power, and the heat and light waves no longer enter the substance, but are almost totally reflected, as in metals, whence the name, "bands of metallic reflection." For metals, "electrical conductors," the absorption coefficient

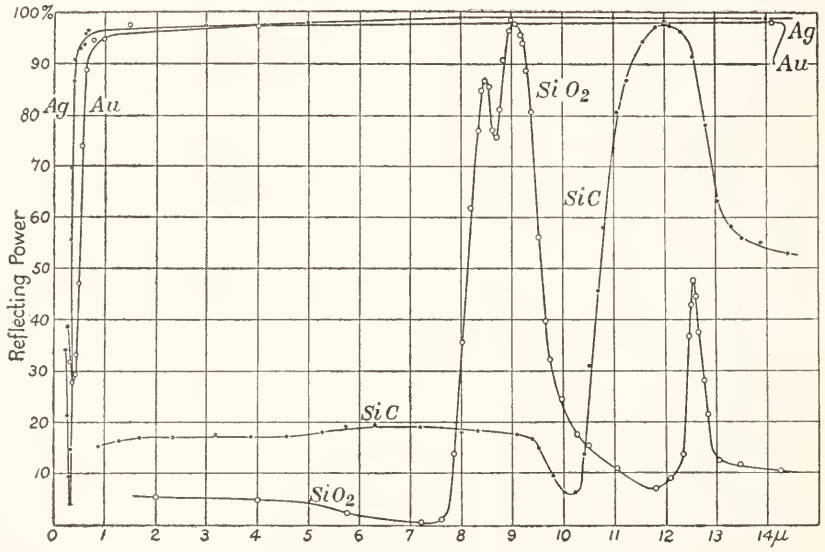

Fig. 24. — Reflecting power; gold, silver, quartz, carborundum.

is so large that nearly all the energy for all (gold and silver are exceptions) wave-lengths is reflected. In other words, the reflecting power of plane surfaces ("regular reflection") of "transparent media" (electrical non-conductors) will be low in all regions of the spectrum, except where there are bands of "metallic reflection." It is evident that the diffuse reflection from rough surfaces of transparent media must also be selectively reflecting. For electrical conductors the reflecting power is high throughout the infra-red spectrum. The great dissimilarity in the reflecting power of these two classes of substances is well illustrated in fig. 24, which contains the graphs of the reflecting power of gold, silver, quartz, and carborundum.

Apropos of the illustration just quoted, of the reflection from smoked glass, Very[1] "records that the percentage of reflected rays, as measured by

[1] Very: Astrophys. Jour., **8**, p. 278, 1898.

the bolometer, is especially large (perhaps two or three times the usual proportion) in the narrow crescent moon where the rays suffer a grazing reflection at a large angle of incidence, the emission under the corresponding angle of emission being small." This is particularly noticeable in the early forenoon. Very's[1] recent discussion gives the impression that, in the moon, "specular reflection" is something to be sought for at the angle of reflection with the sun, at which the image of the sun in rays of 8.5 to 10 μ may be isolated by using a screen with a pinhole aperture. Here "specular reflection" appears to be used in the sense of "regular reflection." The writer is not discussing this limiting case, but it appears self-evident that a matte surface like a plane surface can be selectively reflecting, and hence that a surface of quartz, for example, which, if smooth, reflects like a metal for wave-lengths 8.5 and 9.03 μ and like a transparent medium for all other wave-lengths, must still reflect selectively when it is rough.[2] Hence, in the stream of energy reflected in any direction the density will be greatest for wave-lengths 8.5 to 9.03 μ. Of course these bands of "metallic reflection" will now be less intense. Since the energy density in every direction must be greatest for wave-lengths 8.5 to 10 μ, one would expect to detect this difference in any direction, and not simply at the angle of regular reflection.

If, then, the eye were sensitive to the infra-red quartz would have a "surface color" corresponding to wave-lengths 8.5 and 9.03 μ. In speaking of surface color, however, a sharp distinction must be made, for the reflecting power of these bands is as great as that of metals, although the substance is a non-conductor; whence one would expect the reflecting power to be low. In the case of transparent non-conductors the surface color is due less to reflection than to absorption, for it is due to absorption that the reflected light is deprived of some of its constituents and becomes colored. However, on the long wave-length side of the absorption band the reflecting power is high, which contributes to the color. For example, the aniline dyes, such as fuchsine, have a low reflecting power (as compared with metals) and yet they possess surface color. Pigments belong to the class of substances having "body color." On the other hand, metals, such as gold and copper, also have a surface color, due to selective absorption. They are electrical conductors, however, and theoretically would totally reflect all radiations for all wave-lengths. This has been established

[1] Very: Astrophys. Jour., 24, p. 351, 1906. Here the writer is quoted as having found "that common minerals reflecting diffusively" from 4 to 8 μ have bands of metallic reflection from 8 to 10 μ.

This quotation is erroneous. The writer found that the reflection was "regular" for all wave-lengths, but that from 4 to 8 μ the reflecting power is low, as in cases of transparent media having low refractive indices, while from 8 to 10 μ the reflecting power is high, like metals, hence called "metallic reflection."

[2] See footnote, p. 146, for experimental evidence supporting these statements.

for long wave-lengths.[1] The reflection curves of such metals as gold and silver, however, are entirely different from those of the electrical non-conductors (see fig. 24). In the former the extinction coefficient is always high, while in the latter the extinction coefficient fluctuates through a great range. In quartz the ions have a proper period of undamped electrical vibration which almost totally reflects the wave trains in the region of 8.5 and 9.03 μ, while for the shorter wave-lengths the vibration periods are more damped, the reflection is enormously decreased, and more of the energy is absorbed. In the case of a reflecting surface composed of electrically non-conducting material, of the total energy falling on the surface, the reflected energy in and near the visible spectrum will consist of that reflected from the surface and that part which enters the particles and is returned, due to internal reflection. In the region of 8 to 10 μ (for silicates) almost all the observed energy will be reflected from the surface, and hence none will be reëmitted due to internal reflection. As a whole, then, what the writer found is that the silicates reflect like "transparent media" for all wave-lengths up to 8 μ and like metals from 8.5 to 10 μ. In other words, it may be said that in quartz (SiO_2) the silicon ions retain the proper period of undamped electrical vibration which they would have in the metal, silicon, for wave-lengths 8.5 and 9.03 μ, while, for all other wave-lengths, the vibration periods are more damped and the reflecting power is decreased.

[1] Hagen and Rubens: Ann. der Physik, **8**, p. 1, 1902.

PART VI.

INFRA-RED TRANSMISSION SPECTRA.

CHAPTER I.

INTRODUCTION.

With the accumulation of data the evidence becomes more and more convincing that there are no strong bands of selective absorption (except in the colored glasses given on a later page) in the region of short wavelengths, near the visible spectrum, such as are to be found beyond 6 μ. Material suitable for investigation is obtained with difficulty. The present contributions to the subject of transmission spectra is rather meager in volume, but several of the substances show peculiarities worth recording.

The apparatus and methods of examining the following material, consisting of a rock-salt prism and mirror spectrometer, were described in Carnegie Publication No. 65. Instead of the radiometer, an improved Rubens[1] thermopile was used to measure the energy in the transmission spectra.

GROUP I: TRANSMISSION SPECTRA OF VARIOUS SOLIDS.

MOLYBDENITE (MoS).

(From Yorkes Peninsula, South Australia. Foliated, distorted; thickness, $t=0.05$ and 0.31 mm.; fig. 25.)

In the preceding work it was noticed that the sulphides are, in general, quite transparent. Sphalerite (ZnS) was found to have wide absorption

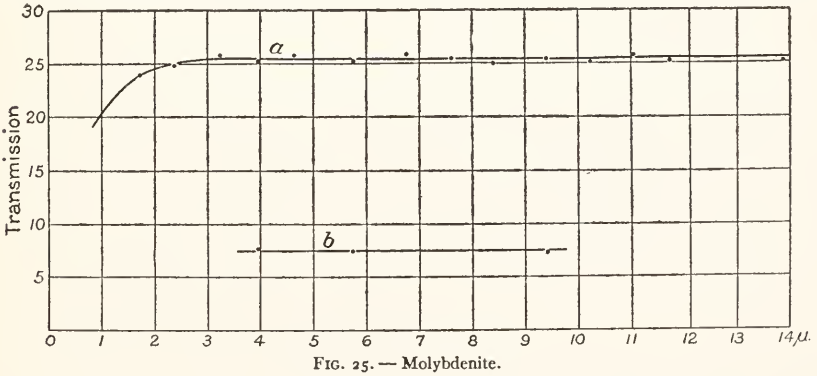

FIG. 25. — Molybdenite.

bands at 3 and 15 μ. On the other hand, stibnite (Sb_2S_3) is opaque to the visible and has a second absorption band beyond 15 μ. In the interven-

[1] See Appendix II.

ing part of the spectrum the absorption coefficient is very small, and the loss of energy is due to the high reflecting power, which is about 40 per cent.

Molybdenite differs from stibnite in that it is very opaque throughout the spectrum, examined to 15 μ. The two specimens examined were thin folia, only 0.05 and 0.31 mm. in thickness (curves *a* and *b*, fig. 25). From the greatly decreased transmission of the thicker piece, it will be noticed that the loss of energy is due to absorption rather than reflection. The absorption coefficient has not been computed, but an inspection of the curves shows that it must be large. By increasing the thickness six times the transmission is decreased 18 per cent, while in stibnite, by increasing the thickness five times, the transmission is reduced only about 5 per cent, in the region of general absorption.

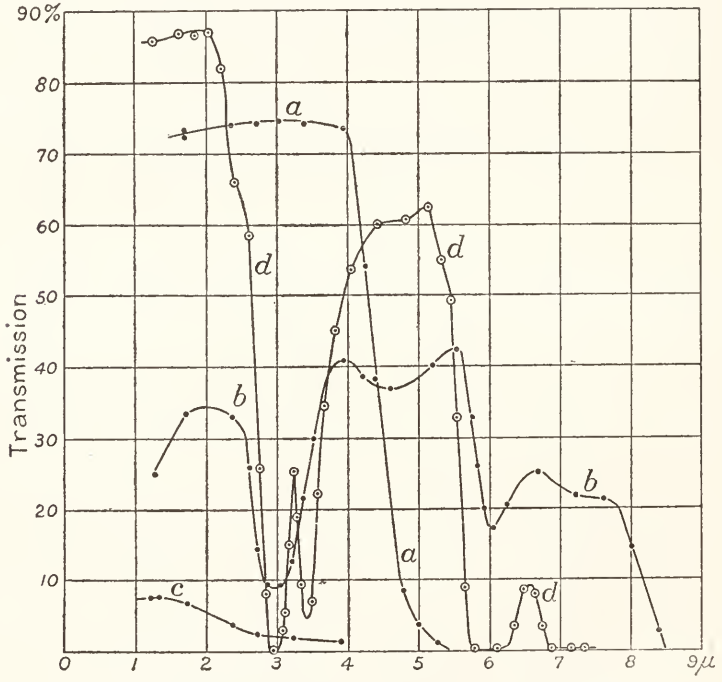

FIG. 26. — Kuntzite (*a*); Cryolite (*b*); Carborundum (*c*); Nitrocellulose.

KUNTZITE [$LiAl(SiO_3)_2$].

(From Pala, California. Cleavage piece, parallel to *m*; transparent; $t = 1.05$ mm. Curve *a*, fig. 26.)

This mineral, which is violet spodumene, is obtainable in large specimens, hence it was of interest to determine its transparency to infra-red radiation. It is lacking in the small band of SiO_2 at 2.95 μ and is more opaque than quartz in the region of 1 μ, so that it would not be more serviceable than the latter in optical work.

CARBORUNDUM (SiC).

(Artificial product; $t = 1.27$ mm. Curve *c*, fig. 26.)

The specimen examined was a flat crystal which transmitted blue light, and reflected yellowish-green light. It has remarkable optical properties,[1] especially a high value for the refractive index. It is opaque in the ultra-violet (Jewell) and beyond 2 μ in the infra-red. In this respect the transmission curve *c*, fig. 26, is very remarkable as compared with all the other substances examined, of which only one, viz, mellite, is as opaque to infra-red rays. The reflection curve was examined previously; it also shows remarkable properties.

CRYOLITE ($3NaF \cdot AlF_3$).

(From Ivigtut, Greenland. Massive, semitranslucent; $t = 2.3$ mm. Curve *b*, fig. 26.)

From the composition of the material it was hoped to find this to be more transparent to heat rays than usually has been the case with minerals. Possibly a pure crystal of cryolite would be different. From the absorption bands (curve *b*, fig. 26) it will be noticed that this specimen contained water of crystallization.

Thomsenolite ($NaLiAlF_6 + H_2O$), previously examined, is an alteration product of cryolite, and from the similarity of the transmission curves it would appear that this sample of cryolite had already undergone some alteration into the hydrated mineral.

NITROCELLULOSE (TRANSPARENT "CELLULOID").

(Curve *d*, fig. 26; $t = 0.138$ mm.)

Transparent celluloid is a mixture of nitrocellulose [$C_{12}H_{16}(NO_2)_4O_{10}$] and camphor ($C_{10}H_{16}O$). The transmission curve which was obtained with a fluorite prism and bolometer is conspicuous for two regions of great absorption, with maxima at 3 μ, 3.43 μ, and 6 μ.

Camphor is a very complex carbohydrate. Its alcoholic properties, OH groups, should cause an absorption band at 3 μ (2.95 μ in Carnegie Publication No. 35, p. 58, for rock-salt prism). Its ketone properties, CO groups (perhaps aldehyde properties, CHO groups), should cause a strong band at 6 μ. Excellent examples of OH groups are (see Carnegie Publication No. 35, p. 108) carvacrol and thymol, of CHO groups are benzaldehyde, cuminol, eucalyptol, colophonium, and venice turpentine, and of both these groups is terpineol. The band at 3.43 μ is characteristic of the CH_3-groups.

Excepting in intensity, the transmission curve is similar to that of collodium (Carnegie Publication No. 65, p. 60), which is also a complex compound of cellulose. It seems rather remarkable that the characteristic vibration period of these groups of atoms is not affected by the complexity of the compound.

[1] Jewell: Physical Review, 24, p. 239, 1907.

SIDERITE ($FeCO_3$).

(From Allevard, France. Cleavage piece; $t = 1.2$ mm.; grayish color; translucent to transparent. Fig. 27.)

This specimen was examined in connection with the carbonates previously studied. The complex band, with maxima at 3.4, 3.9, and 4.6 μ, is in common with the other carbonates. In a very thin section of calcite

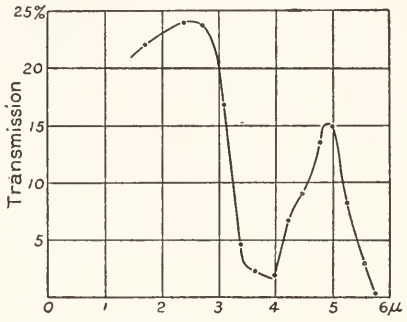

FIG. 27. — Siderite.

($CaCO_3$) this region was resolved into sharp bands, having maxima at 3.44, 3.93, and 4.6 μ. This sample furnishes additional proof that the large groups of chemically homologous compounds have similar absorption spectra.

WULFENITE ($PbMoO_4$).

(From Red Cloud Mine, Yuma County, Arizona. Deep-yellow color; $t = 2.1$ mm. Curve *a*, fig. 28.)

This mineral is of interest in connection with a study of the oxides, *e. g.*, TiO_2, SiO_2, etc. The transmission curve *a*, fig. 24, shows wide

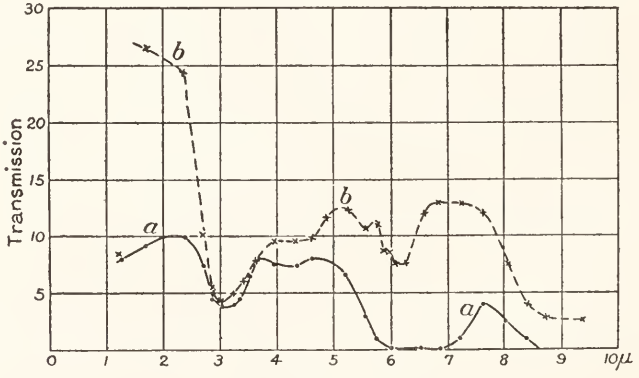

FIG. 28. — Wulfenite (*a*); Phosphorus.

absorption bands at 3.15 and 6.5 μ, and complete opacity beyond 9 μ, where there is a band of metallic reflection.

PHOSPHORUS (P).

(Solid film melted between plates of fluorite. $t = 0.8$ mm. (?). Curve *b*, fig. 28.)

Phosphorus was examined in order to answer an inquiry whether it could be used for prisms contained in vessels with quartz or fluorite windows. The yellow stick phosphorus was used. It was melted under water (at 44° C.), poured on a glass plate, and pressed into a thin sheet by means of a second plate of glass. This thin sheet was then placed between two plates of fluorite and the edges covered with soft wax. As will be noticed in curve *b*, fig. 28, the transmission curve shows bands due to water which adhered to the phosphorus. The latter melted during the latter part of the examination. The transmission curve includes the fluorite plates, which were not clear, and hence increase the observed absorption.

QUARTZ (SiO_2).

($t = 3$ mm. Curve *b*, fig. 29.)

The sample examined was used as a window on the spark-tube in the emission spectra of metals in hydrogen, Part VII. The curve shows that emission lines, if of appreciable intensity, would be transmitted out to 4 μ.

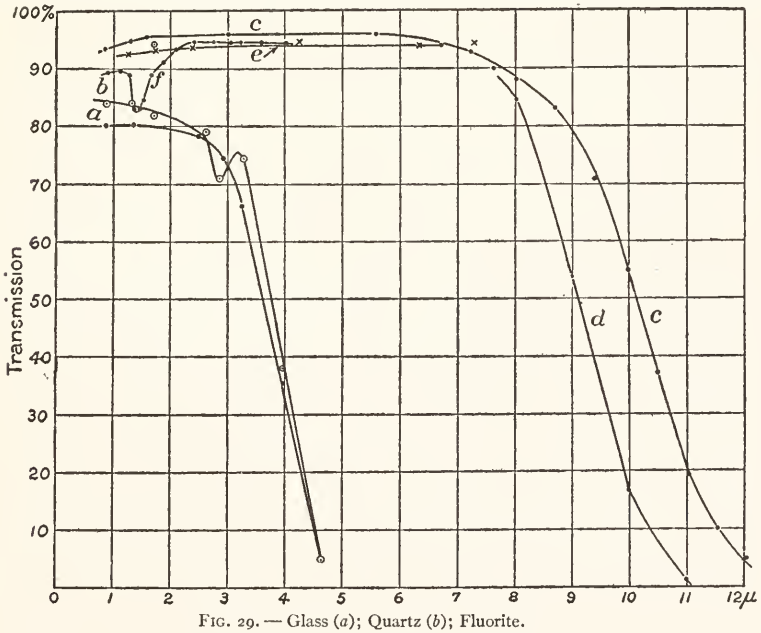

FIG. 29. — Glass (*a*); Quartz (*b*); Fluorite.

GLASS.

(Thickness = 0.75 mm. Curve *a*, fig. 29.)

This sample was examined in connection with prospective work on radiation from incandescent lamps. The transmission is uniform (80 per cent) out to 2 to 2.4 μ. From this it will be seen that the maximum of the energy spectrum of the filament will not be affected by the glass bulb.

FLUORITE (CaF).

(Curve *c*, $t = 2.28$ mm.; curve *d*, $t = 10$ mm.; curve *e*, $t = 1.84$ mm.; curve *f*, $t = 3.85$ mm. light-green color; fig. 29.)

On account of the increased scarcity of this material, it is of interest to determine the effect of inclusions upon the transmission. In fig. 29, curve *c* was a perfectly clear specimen; while curve *e* contained numerous small inclusions, or, perhaps more exactly, small cleavage planes. The latter when held at a distance of 30 to 50 cm. from the eye appeared quite blurred. Nevertheless, throughout the infra-red the loss of energy is only about 2 per cent greater than that of clear fluorite. This is to be expected; for each cleavage plane reflects some of the light, and the magnitude of this reflection, since it depends upon the refractive index, decreases with increase in wave-length. Curve *f* shows the transmission of a specimen of light yellowish-green fluorite (see Carnegie Publication, No. 65, p. 69, for another example) which has an absorption band at 1.4 μ, hence not suitable for a prism. This specimen was free from inclusions.

CARBON (C).

(Curves *a*, *b*, *c*, lampblack; curve *d*, diamond; fig. 30.)

The commonest and most conspicuous example of the effect of structure upon absorption is to be found in carbon in the form of lampblack and

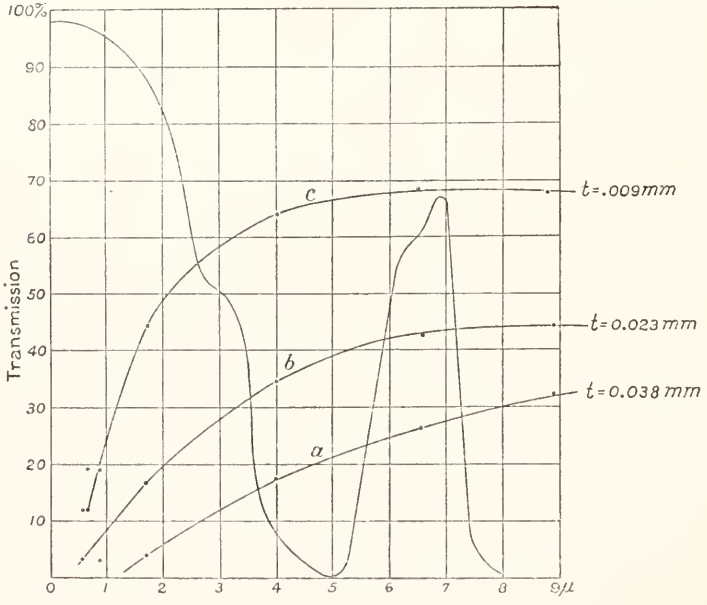

FIG. 30. — Carbon (*a*), (*b*), (*c*); Diamond.

of diamond. Since the observations on these two substances are published in separate and rather isolated places they are incorporated here for completeness of illustration of the effect of structure. The transmission curves

a, *b*, *c*, thickness 0.038, 0.023, and 0.009 mm., respectively, of lampblack are due to Ångström.[1] The transmission curve of diamond is due to Julius.[2] The lampblack is opaque to the visible and shows an increase in transmission with wave-length. The diamond crystal is transparent to the visible and has well-defined absorption bands at 3, 4, and 5 μ and complete opacity beyond 8 μ. A band of metallic reflection is predicted at 12 μ, which happens to coincide with the band of carborundum.

It seems rather remarkable that diamond should have one of its principal absorption bands in the region where carbohydrates have a wide band of great transparency.

GROUP II: TRANSMISSION SPECTRA OF VARIOUS SOLUTIONS.

The data presented here were obtained several years ago (but not published) in connection with an investigation of methods of measuring radiant efficiencies.[3] One of the methods of measuring the efficiency of an illuminant, *i. e.*, the ratio of the light emitted to the total radiation, is to absorb the infra-red by means of a water cell. The idea persists even to this day that a water solution of potassium alum absorbs more heat than does clear water, although Donath and others demonstrated, long ago, that this is not the case; the data herewith presented is further proof of this fallacy. During the present year (Phys. Zeitschrift, 1907) measurements of radiant efficiencies have been made using a water solution of ammonium-iron alum, and it was claimed that the solution was more opaque than pure water. A transmission curve of this substance will be shown presently which indicates a greater opacity than water. The iron alum oxidizes readily and it is difficult to keep the solution clear.

The problem was recently presented to the writer by the Astrophysical Observatory to suggest a substance (see asphaltum) that absorbs all the visible or all the infra-red energy, the dividing line being 0.76 μ. Such a substance would of course be an ideal energy filter; but no such substance is known. Indeed, from all the substances examined, it appears that none (at least none of the common ones) have large absorption bands near the visible. Beryl[4] is recorded as having a large band at 0.89 μ, when examined in polarized light. Cyanine would be a fairly good material for absorbing the visible, but it is very opaque in the region of 6 to 8 μ. Iodine would be much better material for absorbing the visible, and transmitting the infra-red. Its absorption band, at about 7.3 μ, is very weak. The absorption band of iodine in the visible spectrum corresponds closely with the sensibility curve of the eye. Since we are concerned only with the light that affects the eye, the fairest rating of efficiencies would be to com-

[1] Ångström: Wied. Annalen, **36**, p. 717, 1889.
[2] Julius: Königkl. Akad. Wiss. Amsterdam, Deel I, No. 1, 1892.
[3] Nichols & Coblentz: Phys. Rev., **17**, p. 267, 1903.
[4] Königsberger: Ann. der Phys. (3), **61**, p. 687, 1897.

pare the energy that affects the normal eye to the total energy. This would lower the present efficiencies of sources that are rich in the red, which color affects the eye but little.

The use of iodine in solution is prohibited by the selective absorption of heat rays by all known solvents. On the other hand, solid iodine evaporates readily, so that it would be impossible to keep a solid film of uniform thickness for any great length of time.

ASPHALTUM.

(Curve c, $t=0.1$ mm ; $a=0.0005$ mm.; $b=0.03$ mm.; $d=0.005$ mm.; fig. 31. For the complete curve, to 14 μ, see Carnegie Publication No. 35, p. 75, and fig. 44, p. 198.)

The next best substance to iodine for absorbing the visible and transmitting the infra-red is asphaltum, which is a solid hydrocarbon, previously examined. This substance can be formed into films of any desired thickness. In fig. 31 curves a and b are due to Nichols.[1] From the curves it

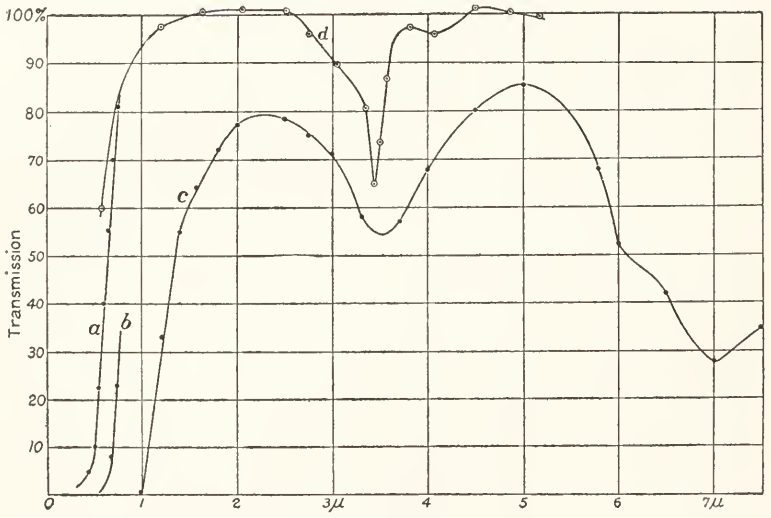

FIG. 31. — Asphaltum.

will be seen that a thickness can be selected which fulfills the conditions of complete transparency beyond 0.7 μ better than any other common substance. Even the thick film (curve c, $t=0.1$ mm.), which transmitted a trace of red, shows great transparency, after passing beyond the effect of the absorption band in the visible. A film absorbing up to 0.65 or 0.7 μ would be practically transparent in the infra-red (see Carnegie Publication No. 35, p. 17), where, for a very thin film of water, the small absorption band at 4.75 μ, similar in intensity to those of asphaltum, has entirely disappeared. By using a clear rock-salt plate, covered on both sides to prevent the action of moisture, a fair standard could be produced. The

[1] E. L. Nichols: Phys. Rev., **14**, 204, 1902.

asphaltum may be applied to the rock-salt as a thin varnish, the volatile parts of which evaporate in a short time.

Asphaltum varnish, applied in an extremely thin coating, forms an excellent protecting surface for radiometer or radiomicrometer windows made of rock-salt. It might also be used advantageously as a covering for rock-salt prisms to protect them from moisture. The pair of films of asphaltum to be used for such purposes can be made extremely thin, and are almost transparent, as shown in fig. 31, curve *d*, which was of a light amber color showing but little absorption in the visible spectrum. The film was prepared from commercial asphaltum varnish, which is a very thick solution, by diluting it with gasoline. This precipitates the very insoluble constituents, which apparently are simply held in suspension, and by experimenting on the amount of gasoline to be added, a film or pair of films of any desired thickness may be produced by a single dipping of the plate or prism. Of course, a thicker film may be formed by using a thicker solution, or by applying several coats of the thin solution. By filtering the dilute solution through cotton wool or through filter paper the black insoluble asphaltum particles are removed. The dried film is then homogeneous and perfectly free from even traces of black particles. The gasoline must be quite free from moisture, otherwise there is likely to be a slight action on the rock-salt surfaces, and the dried film will not be so homogeneous as that obtainable on a glass plate. It may be possible to apply a homogeneous film of paraffin or of ozokerite, which is white, and which, on account of its low refractive index, will reflect less than a rock-salt surface; but neither of these substances are as satisfactory as asphaltum purified, as indicated above. Such surface coverings for hydroscopic substances are, of course, useful only where the radiometer and prism are used in making relative comparisons, *i. e.*, it is not adapted to making spectral energy measurements of sources of radiation, where the absorption of the apparatus and the atmosphere must be eliminated.[1] Curve *d* is for two films on a plate of glass, 0.175 mm. thick. The values are obtained by dividing the observed transmission, when the glass was coated with asphaltum, by the observed transmission through the clear glass. The fact that the transmission is greater than 100 per cent is due to the higher reflecting power of glass, for which no correction was made.

[1] Since writing this, Dr. A. Trowbridge, at the Washington Meeting of the American Physical Society, April, 1908, described the transmission of extremely thin films of collodium (Carnegie Publication No. 65, p. 60, fig. 46) and their application to rock-salt as a protecting surface. For the region of the spectrum up to 6 μ there are no prominent absorption bands, and the small ones at 3.3 μ have almost entirely disappeared in the thinnest films, which are of the order of a light-wave in thickness. Collodium is said to be slightly hydroscopic, but whether it is sufficiently so to become separated from the rock-salt is unknown. At this meeting it was learned that at the Astrophysical Observatory it is proposed to use asphaltum varnish to protect the large rock-salt prism which is about 18 cm. high.

ALUM SOLUTION.

(Saturated solutions at 0° C.; cell 1 cm. thick; fig. 32.)

In fig. 32 are given the transmission spectra of water (o–o–o–o) and of solutions of the alums of potassium (x–x–x), ammonium (•–•–•–•), and of ammonium-iron. The curves are due to E. F. Nichols[1] and are included here because of their bearing upon the present data. The transmission curves of the solutions of potassium and of ammonium alum are identical with that of water. The ammonium-iron alum $[(NH_4)_2Fe_2(SO_4)_7]$

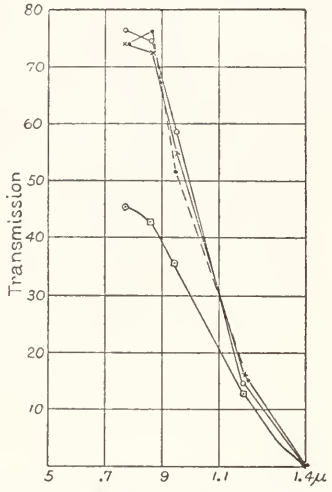

FIG. 32. — Water o–o–o; Potassium alum x–x–x; ammonium alum •–•–•–•; ammonium iron alum (lowest curve).

shows greater opacity, which from the trend of the curve appears to extend into the visible spectrum, due perhaps to a trace of iron oxide which is avoided with difficulty. The transmission curve of a clear plate of alum 4 mm. in thickness is shown in curve *a*, fig. 33.

BORAX AND POTASSIUM PERMANGANATE.

(Cell 1 cm. thick; glass walls; fig. 33.)

In fig. 33 are given the transmission curves *b* of borax ($Na_2Br_4O_7$) and curve *d* of potassium permanganate ($KMnO_4$). The latter solution was not saturated. The results show that there is no increased absorption of the solution over that of pure water, except in permanganate, which, of course, is almost opaque to the visible.

LANTHANUM NITRATE ($LaNO_3$); DIDYMIUM NITRATE $[Pr,Nd(NO_3)_3]$; SULPHURIC ACID (H_2SO_4); LIQUID GLASS (Na_2SiO_3).

(Cell 1 cm. Concentration of nitrates unknown. Fig. 34.)

In fig. 34 are given the transmission curves, *a* of sulphuric acid, *b* of lanthanum nitrate (solution), *c* of didymium nitrate (solution), and *d* of

[1] E. F. Nichols: Phys. Rev., 1, p. 1, 1896.

liquid glass. The sulphuric acid is more transparent than water, while the didymium nitrate has a sharp absorption band at 0.76 μ. The latter

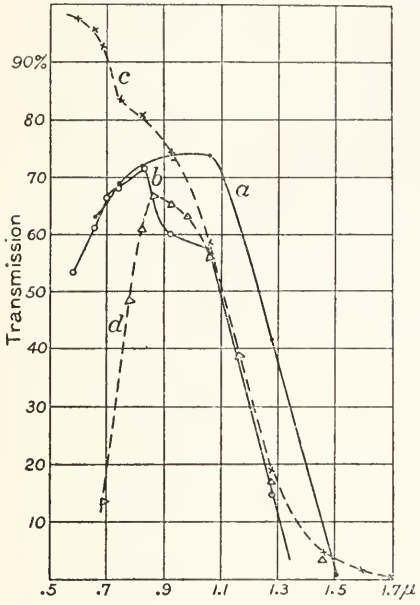

FIG. 33. — Potassium alum (*a*); Borax solution (*b*); Water (*c*); Potassium permanganate solution.

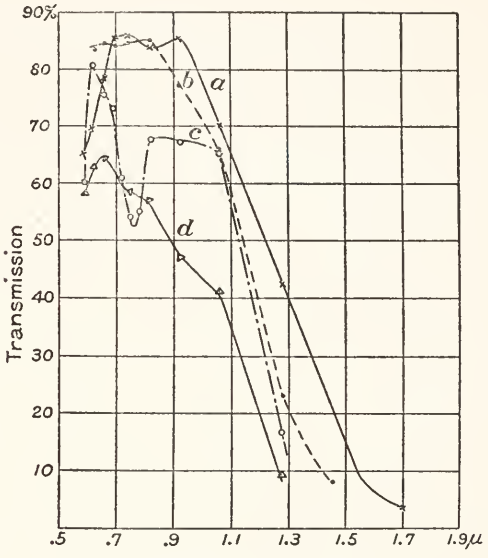

FIG. 34. — Sulphuric acid (*a*); Lanthanum nitrate (*b*); Didymium nitrate (*c*); Liquid glass.

have absorption bands in the visible, so that they would not be useful for efficiency work. The same is true of liquid glass.

CHLORIDES OF THE YTTRIUM GROUP (Sc, Yt, La, Yb); NEODYMIUM NITRATE [$Nd(NO_3)_3$].

(Cell 1 cm. Concentration unknown. Fig. 35.)

These solutions, like the preceding ones, were obtained from the Chemical Laboratory of Cornell University, and the concentration was unknown. They were examined to learn whether the sharp absorption bands in the visible are also to be found in the infra-red. It will be noticed that the didymium nitrate (curve *b*, fig. 35) has two bands at 0.78 and 0.98 μ, while the yttrium group of chlorides have a band in common with didymium at 0.98 μ.

GROUP III: TRANSMISSION SPECTRA OF COLLOIDAL METALS.

The metals and non-metals present two distinct types of absorption, of reflection and of emission spectra. The metals (electrical conductors), even in very thin films, are extremely opaque to all radiations throughout the spectrum, except gold, silver, and copper, which have narrow transparent bands at 0.32, 0.5, and 0.6 μ, respectively.[1] The opacity is really due to

[1] Hagen & Rubens: Ann. der Phys., **8**, p. 432, 1902; Javal: Ann. de Chim. et Phys. (8), **4**, p. 137, 1895.

their high reflecting power, which is uniform throughout the infra-red. Their emission (arc and spark) spectra consist of numerous fine lines, which occur throughout the visible and ultra-violet part of the spectrum.

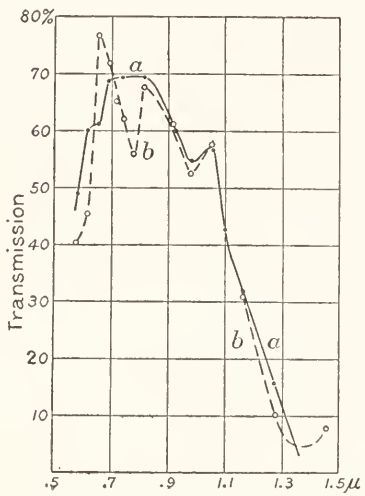

FIG. 35. — Chlorides of Yttrium Group (*a*); Neodymium nitrate.

No strong lines have yet been found in the infra-red, except in the alkali metals. On the other hand, the non-metals (insulators) have absorption bands throughout the spectrum. Their reflecting power is low, and in some compounds is highly selective in the infra-red. They have emission lines which extend far into the infra-red. The elements on the border line between metals and non-metals are of peculiar interest, and the reflecting power of their compounds deserves further study. A notable example is silicon, which from the known properties of non-metals would be expected to have a uniformly low reflecting power throughout the infra-red; in the form of a compound, SiO_2, the reflecting power at 8.5 and 9 μ attains a value as high as that of metals. The elements iodine, selenium, and sulphur have a uniformly low reflecting power. It would be interesting to learn whether only the compounds of non-metals have bands of selective reflection in the infra-red; all of our present data indicate that only in a compound (*cf.* SiO_2) do the ions of non-metals attain a freedom such as obtains in metals.

SILVER.

(Colloidal film, on glass. Curve *b*, fig. 36.)

The film examined was made[1] by Prof. R. W. Wood, and was of a deep ruby-red color. In fig. 36, curve *b*, is given the transmission curve of a thin uniform film of colloidal silver, deposited on glass. The transmission begins in the red, and increases uniformly throughout the infra-red to 4 μ, beyond which it was not possible to extend the observations on account of the opacity of the glass. This is exactly the reverse effect observed with a metallic film (see fig. 24), where the transparency lies in the violet and the opacity extends throughout the infra-red. The film of colloidal silver behaves like a turbid medium, which has the property of increasing in transparency with wave-length. This is in agreement with Garnett,[2] who concludes from the optical properties of Cary Lea's so-called solutions of allotropic silver that they consist of small spheres of silver, *i.e.*,

[1] Cary Lea's Allotropic Silver, Amer. Jour. Sci., vol. **37**, p. 746, 1889.

[2] Garnett: Proc. Roy. Soc. (A), **76**, p. 370, 1905–06; Phil. Trans., A, pp. 385–420, 1904.

normal silver in a finely divided state, little if any being in true solution (molecularly subdivided). He further concludes that the color of ruby gold glass is due primarily to the presence of small spheres of gold; the irregular blue and purple colors, sometimes exhibited by gold glass, are then explained by the presence of crystallites (caused by the coagulation of gold spheres) which reflect but do not transmit red light.

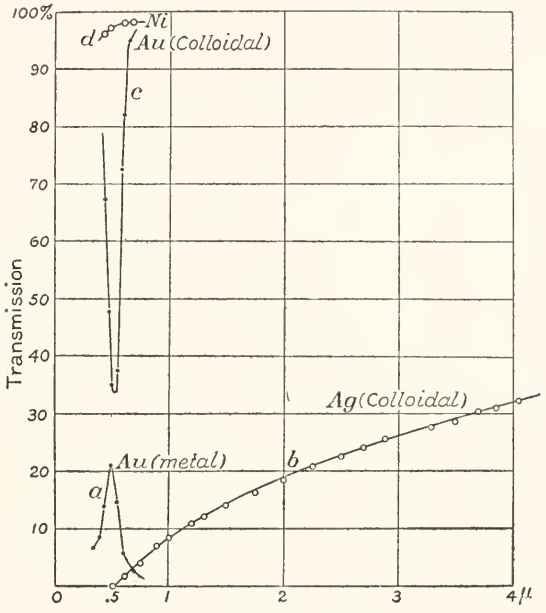

FIG. 36. — Gold; Silver; Nickel.

MARINE BIOLOGICAL LABORATORY WOODS HOLE LIBRARY MASS.

In view of the fact that colloidal metals appear to behave exactly the reverse of films of a metal in the normal state, the subject deserves further consideration.

GOLD AND NICKEL.

In fig. 36, curve *a* gives the transmission (Hagen and Rubens, *loc. cit.*) of a metallic film of gold, which has the well-known transmission band in the yellowish-green part of the spectrum. Curves *c* and *d* give the transmission of suspensions, in water, of colloidal gold and nickel, respectively, studied photometrically by Ehrenhaft.[1] The gold transmitted red, while nickel (also Pt and Co) have a brown color by transmitted light. As in the present work, the behavior of the colloidal material is exactly the reverse of the normal metal film, thus placing it under the class known as non-metals or "insulators."

[1] Ehrenhaft: Ann. der Phys., 11, p. 489, 1903.

GROUP IV: TRANSMISSION SPECTRA OF COLORED GLASSES.

Cobalt Glass.

(Fig. 37. Thickness, 2.43 mm.)

Colored glasses have been but little studied. Nichols[1] examined cobalt glass, and found an absorption band at 1.4 μ. This is one of the few substances having a prominent band near the visible spectrum. Garnett (*loc. cit.*) concludes that the deep blue color of cobalt glass can not be due to small diffused spheres of metallic cobalt, which would give a reddish color to transmitted light, but that the metal is in the form of discrete molecules (amorphous).

For the present work a fluorite prism and bolometer were used (see Appendix II).

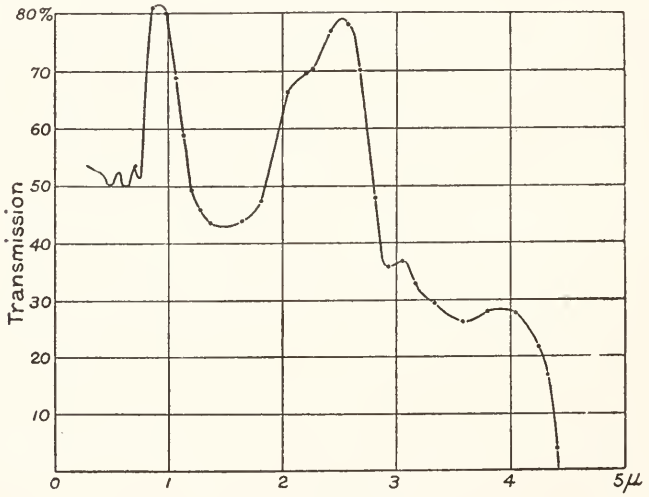

Fig. 37. — Cobalt blue glass.

In fig. 37 is given the transmission curve of a cobalt blue glass which showed three weak absorption bands in the visible spectrum. In the infra-red there is a larger absorption band at 1.5 μ, a smaller band at 2.1 μ, and second large band at 3.5 μ. The small band at 3 μ is due to the glass itself, and is also found in quartz. Beyond 4 μ the opacity is due to the glass, as found in clear specimens.

The behavior of this glass is entirely different from the red glasses to be noticed on a following page. It is not like an optically turbid medium, unless we consider it to have more than one region of selective absorption, which is in line with the conclusion arrived at by Garnett (*loc. cit.*).

[1] Nichols, E. F.: Phys. Rev., 1, p. 1, 1893.

Blue-violet Glass.

(Schott's[1] No. F 3086; $t = 2.58$ mm.)

In fig. 38 is given the transmission of a plate of blue-violet glass. There is a large absorption band at 0.5 to 2 μ, followed by smaller bands at 2.1 and 3.5 μ. In the deep infra-red such a band would cause selective reflection. In the present case the absorption band is due to the metal behaving somewhat like an optically turbid medium. Using a pocket spectroscope close to a Nernst glower, it was found that a trace of yellow

Fig. 38. — Blue-violet glass.

at 0.56 μ and of red at 0.707 μ was transmitted, the intensity of the maxima being of the order of 0.01 per cent. In the violet the transmission was 30 per cent. This region was studied with a spectrophotometer. Ångström has very ingeniously applied this glass in measuring the violet radiation from the sun; using an absorption cell of water, 1 cm. thick, in addition to this glass plate, all the radiation beyond 0.5 is absorbed.

Green Glass.

(Schott's copper oxide, No. 431 III. Fig. 39. Thickness $t = 3.43$ mm.)

The specimen examined showed an absorption band in the violet and a second one in the red. There appears to be a small band at 2 μ, beyond which point there is the usual absorption of uncolored glass. The band at 2.95 μ, found in silicates, *e.g.*, mica, seems to be intensified by the presence of coloring substance, while the transmission seems to be terminated at a shorter wave-length (also due to the coloring substance) than would be found in a clear plate of glass of the same thickness.

Ruby Glass.

(Fig. 40. Curve *a*, Schott's monochromatic red, No. 2745; $t = 3.18$ mm.
Curve *b*, impure red; $t = 2.48$ mm.)

The monochromatic red glass examined is used in the Holborn and Kurlbaum pyrometer. The second sample, curve *b*, transmitted impure

[1] See Zsigmondy, Zs. für Instrk., **21**, p. 97, 1901.

red; it was taken from a Le Chatelier pyrometer and is described as a copper oxide glass. Although thinner, the second sample is the more opaque in the region of 1 to 2.5 μ. The transmissivity of the monochromatic red glass is very unusual. In the region of 1 to 2.5 μ the metal which is used to color the glass renders it more permeable to heat waves than is ordinary, visually transparent glass. The band at 2.9 μ appears to be intensified by the presence of the metal, which behaves like the

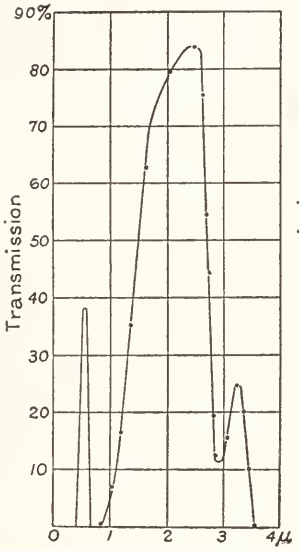

FIG. 39. — Green glass.

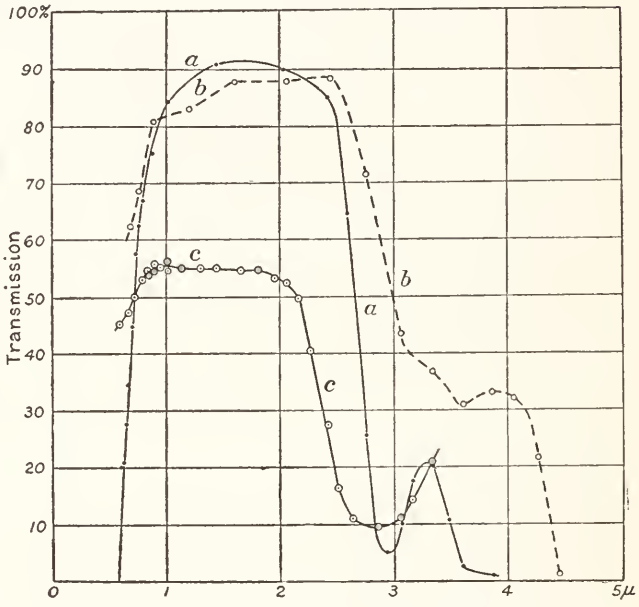

FIG. 40. — Ruby glass (*a*) and (*b*); Sphalerite.

colloidal suspensions just mentioned. In fact, it is a pertinent question whether the red color in glasses is due to the presence of metals, such as copper and gold, in the colloidal condition. The monochromatic red glass was found to have a uniform reflecting power (about 4 to 5 per cent) throughout the spectrum to 8 μ. This seems to show that the transparent region at 1 to 2 μ is not due to the same cause that produces an abnormal transparency on the short wave-length side of a region of anomalous dispersion.

BLACK GLASS.

(Fig. 41. Curve *a*, $t=2.48$ mm.; curve *b*, Schott's Rauchglass No. 444, III, $t=3.6$ mm.)

Curve *a* gives the transmission of a dark "neutral" glass, colored with the oxides of cobalt and nickel. This glass has a uniform absorption throughout the visible spectrum. There are small absorption bands at 2 and 3.5 μ, respectively. Curve *b* gives the transmission of a very dark glass, which shows an absorption band in the region of 1.5 μ.

Considered as a whole, these glasses can be divided into two groups,

viz, (1) glasses having absorption bands in the visible and in the infra-red spectrum, and (2) glasses having a wide absorption band in the optical region, followed by an increase in transparency with wave-length. The red glasses belong to the latter group, and their behavior is more nearly like that of optically turbid media, the color being due to the presence, in the glass, of small spheres of metal (see Garnett, *loc. cit.*). To the first group belong the cobalt blue and Schott's blue-violet glass. If the color in some glasses is due to the metal, one would expect great opacity in the infra-red, as is known for a thin film of the metal. If the metal is present in a colloidal form, the present examination of colloidal silver would indicate great transparency, with the possibility of small absorption bands in the infra-red. The whole question is in an unsettled state, and an investigation of the transmission of various glasses, blown into thin films, as described in Carnegie Publication No. 65, page 65, seems highly desirable.

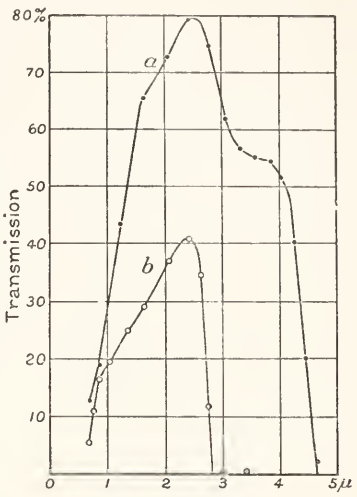

FIG. 41. — Black glass.

In leaving this subject it is of interest to note that a specimen of garnet (Carnegie Publication No. 65, p. 59) was found to have a wide absorption band, with complete opacity extending from 1.2 to 2.6 μ. This is one of the few substances having a large absorption band near the visible spectrum.

SPHALERITE (ZnS).

(Cleavage piece; $t = 1.53$ mm.; transparent; slight yellowish tinge; curve *c*, fig. 40.)

This substance was previously examined (Carnegie Publication No. 65, p. 63), using for the purpose a rock-salt prism and a radiometer. In the present examination, the same mirror spectrometer, but a fluorite prism and a bolometer were used. On account of the small dispersion at 1 μ the rock-salt prism is not well adapted for work in this region. The transmission curve of sphalerite appears to have a band at 1.8 μ. On examination of the original data and curves, it appears that in redrawing the curve for publication the draftsman placed the point at 1.3 μ a little too high (should read 59 per cent), which in the reduced illustration makes a depression at 1.8 μ.

The curve obtained with the fluorite prism is given in fig. 40, and represents conditions more accurately. A Nernst glower was used as a source, which gave large deflections in this region of the spectrum.

The transmission curve increases uniformly from 47 per cent at 0.6 μ to 56 per cent at 1 μ, then decreases uniformly to 54 per cent at

1.8 μ, beyond which the transmission drops rapidly to a minimum at 2.9 μ, previously found. Using this larger dispersion, there appear to be no absorption bands up to 1.9 μ. The study of zinc sulphide is of interest in connection with luminescence of one form of this substance known as Sidot blende. In their study of the rapidity of decay of phosphorescence in Sidot blende, when subjected to infra-red rays, Nichols and Merritt[1] found that the rate of decay was the most rapid when exposed to infra-red rays of wave-length 0.9 μ and of wave-length 1.37 μ. From this it would seem that the screen of Sidot blende possessed broad absorption bands with maxima in the region of 0.9 μ and 1.37 μ. The luminescence of Sidot blende appears to be due to some metal dissolved in it. From the foregoing experiment on sphalerite (ZnS) it appears that these absorption bands are not due to the ZnS, but rather are to be sought for in the dissolved metal (see cobalt glass), and in the cement, in case a glue is used to secure the powder in the form of a "screen." The present study of colored glasses gives us some idea of what to expect in solutions of metals (oxides of metals?) in glasses; while the phenomenon may be further complicated by the molecular structure of ZnS, which in the form of Sidot blende may have absorption bands not found in sphalerite.

[1] E. L. Nichols and E. Merritt: Phys. Rev., **25**, p. 362, 1907.

CHAPTER II.

EFFECT OF SPECIAL GROUPS OF ATOMS OF RADIANT ENERGY.

In the present chapter it is purposed to discuss some of the relations found among the infra-red spectra of the various substances examined; and incidentally to explain some apparently inconsistent statements made in Part I on the effect of certain particular groups of atoms in producing characteristic absorption bands.

COMPARISON OF ULTRA-VIOLET AND INFRA-RED.

Hartley[1] found that an open chain of CH-groups, as well as a union of C and N atoms, produced no absorption bands in the ultra-violet. Neither could he identify any absorption band, of any of these substances, with the carbon atom in the benzene ring; the molecules behaved as though there were no special atoms present. This is just the opposite of what was found in the infra-red. But the length of the infra-red spectrum examined is 60 times as long as the ultra-violet. It is, therefore, possible to find relations in the infra-red which, on account of the narrowness of the spectrum, may not be found in the ultra-violet. In the infra-red there are transparent regions between characteristic absorption bands, which are often several times the width of the entire ultra-violet spectrum. The petroleum distillates (chain compounds) have a wide transparent region between 4 and 5 μ, just as Hartley found in the ultra-violet. In general, if we were to examine a narrow region of the spectrum, *e.g.*, the ultra-violet, or at 4 μ in the infra-red, it appears to be a matter of chance whether or not absorption bands will be found there. In the visible spectrum many substances have absorption bands, *i.e.*, are colored. If the eye were sensitive to rays of wave-lengths 3 to 3.5 μ, all the carbohydrates would appear "colored," and the position of the maximum of the absorption band would be just as irregular as those found in the visible and in the ultra-violet spectrum.

THE HYDROXYL GROUP.

During the preparation of the third volume of Kayser's "Handbuch der Spectroscopie" only the writer's "Preliminary Report on Infra-Red Absorption Spectra"[2] was available to the compilers. They call attention to the fact that "the writer found an effect due to special groups of atoms, particularly OH and CH_3. Although many substances, which contain the

[1] Kayser: Spectroscopy, 3, p. 169 and p. 170.

[2] Coblentz: Astrophysical Journal, 20, 207, 1904.

OH-group, have an absorption band between 2.9 and 3 μ, Coblentz questions whether they are due to the OH-group. On the other hand, he thinks the CH_3-group causes the band at 3.43 μ."

This inconsistency is easily explained. One need but examine the third volume of Kayser's Spectroscopie, pages 81, 83, 84, 88, 283, etc., and see the numerous exceptions to "Kundt's Law," to be convinced that the announcement of that "Law" was premature. Knowing how subsequent investigators were misled by this announcement, it seemed to the writer that, so long as there were any serious exceptions, the effect of special groups of atoms on heat-waves should be doubted until the evidence was much greater than obtained at that time. The mineral brucite [$Mg(OH_2)$] caused this doubt; for if there is an effect due to the OH group, one would expect to find it in such a simple compound as this one. The first examination of brucite showed no band at 3 μ, but a wide band with a maximum at 2.6 μ. Since then this mineral has been re-examined, using a larger dispersion, and the large band was resolved into its components, with maxima at 2.5, 2.7, and 3 μ. In other words, this mineral has the characteristic band of the hydroxyl group. In the meantime, numerous other substances (see Carnegie Publication No. 65) containing OH-groups and water of crystallization have been examined. In Carnegie Publication No. 65, the exceptions to the rule that the OH-group has a characteristic absorption band at 3 μ were found among minerals of which the chemical constitution is in doubt. The absorption band at 3 μ, found in substances containing hydroxyl groups, is, therefore, to be ascribed to that group of atoms. The band at 3 μ found in the alcohols belongs, therefore, to the OH-group, and one ought not expect (as the writer stated in Carnegie Publication No. 35, p. 108) to find a second band at 6 μ (which is found in water), if the 3 μ band is due to the OH-group. The OH group apparently does not produce a harmonic series of bands such as are to be found in compounds containing CH_2 or CH_3-groups. Water also has a harmonic series of bands, but it has not yet been shown to be due to the OH-group.

THE EFFECT OF MOLECULAR WEIGHT OF THE MAXIMA.

In Part I a search was made for a shifting of the maximum of an absorption band with an increase in the number of atoms, or especially of groups of atoms, in the molecule. The evidence was very contradictory. In the case of the methyl derivatives of benzene, the maximum of the band was found at 3.25 μ in benzene, at 3.3 μ in toluene ($C_6H_5CH_3$), at 3.38 μ in the xylenes [$C_6H_4(CH_3)_2$], and at 3.4 μ in mesitylene [$C_6H_3(CH_3)_3$]. In other words, by substituting three CH_3-groups for an H atom, we have shifted the maximum from 3.25 to 3.4 μ. Several gases showed a shift of the band, in the region of 3.2 to 3.5 μ, toward the long wave-lengths with an increase in the number of H atoms. On the other hand, several nitrogen

derivatives of benzene showed a shift of the maximum toward the short wave-lengths. An examination of two petroleum distillates, C_8H_{18} and $C_{24}H_{50}$, showed no shift of the maxima, and on the whole the evidence of a shift, due to a change in molecular weight, was inconclusive.

In Carnegie Publication No. 65, p. 56, the sulphates showed absorption and reflection bands which seemed to shift toward the long wave-lengths with increase in molecular weight. This data will be discussed in the present paper.

Ever since the announcement of "Kundt's Law" various observers have tried to find relations among the absorption bands, viz, such that with an increase in molecular weight the band shifts toward the long wave-lengths. The results have just been discussed in the first part of this chapter. There is a physical basis for expecting a shift of the band with change in molecular weight. For example, the sulphate of the metals K, Rb, and Cs have been compared by Tutton,[1] who has shown that both as regards crystalline form, specific gravity, thermal expansion, and corresponding refractive indices the Rb salt lies between the K and Cs salts.

In Carnegie Publication No. 65, the sulphates of Mg, Ca, Sr, Cd, and Ba were found to have the maximum of their absorption at 4.5, 4.55, 4.6, 4.6, and 4.63 μ, respectively. The same shifting of the maximum was observed in the reflection bands of $SrSO_4$ and $BaSO_4$; in the former the maxima are at 8.2, 8.75, and 9.05 μ, while in the latter the maxima are shifted to 8.35, 8.9, and 9.1 μ.

In the present paper all the available data have been compiled, to show this shift. In fig. 42 is given a composite of the reflection curves of the carbonates [(Mg, Ca, Zn, Ba, Pb) CO_3] described on a previous page. The maxima are evidently double, although it is not very apparent in some curves. As a whole, however, the location of the maxima of $PbCO_3$ is so much farther in the infra-red than in $MgCO_3$ that there can be no doubt that the shift is a real one.

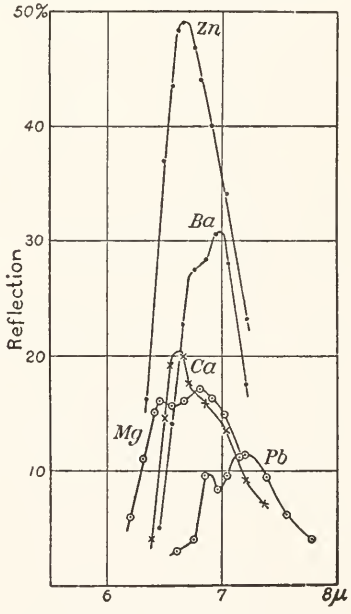

FIG. 42. — Reflection curves of carbonates.

In fig. 43 are given the graphs of the maxima of the *reflection* band plotted against atomic weight of the basic atom in the molecule. The carbonates of Mg, Ca, Zn, Sr, Ba, Fe, Cu, Pb are included. In this figure the two maxima of the complex band at 6.4 to 7.2 μ are plotted. When the

[1] See Miers's Mineralogy.

maximum is not sharp and well defined, several readings were made and plotted in the figures. This method of reading a flat band establishes a limit within which the maximum may lie. The two graphs are approximately parallel, and show a uniform shift of the maxima of Mg, at 6.55 and 6.86 μ to 6.94 μ and 7.18 μ, respectively, in Pb. The carbonates of Fe

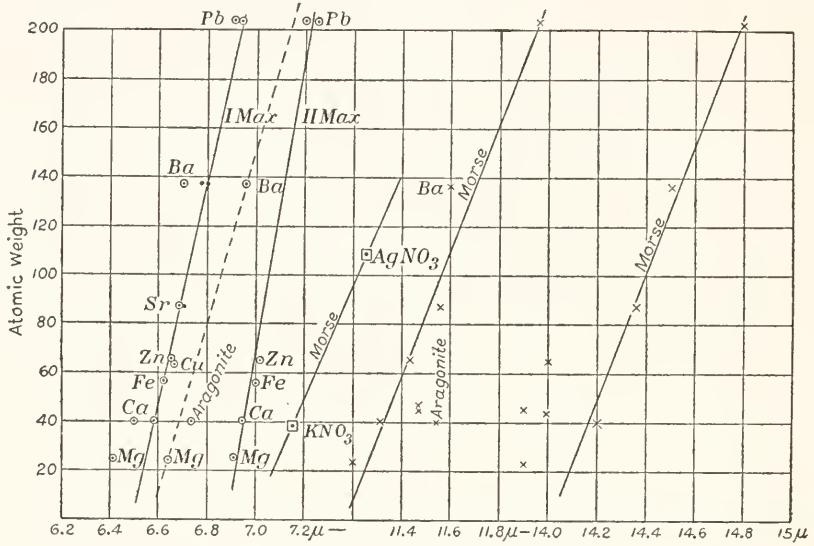

FIG. 43. — Maxima of reflection bands of carbonates.

and Cu lie farthest from the curves; but they belong to a different group in Mendelejeff's table. The graphs at 11 μ and 14 μ are due to Morse, see Appendix III.

In fig. 44 are plotted the maxima of the *reflection* bands of the sulphates [$(H_2, Mg, Ca, Sr, Ba)SO_4$], previously examined (Part IV). Here there are

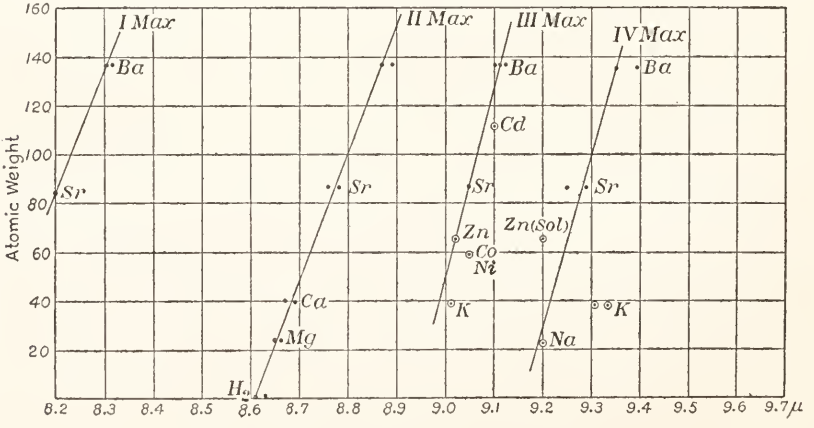

FIG. 44. — Maxima of reflection bands of sulphates.

four bands. As in the preceding, several readings of each ill-defined band are plotted in order to get the limits between which it extends. It is of interest to note that one of the H_2SO_4 bands, at 8.62 μ, falls on the graph of the second maximum.

In fig. 45, the maxima of the *absorption* bands of the sulphates [(Mg, Ca, Sr, Cd, Ba) SO_4] are plotted (see Part III, Carnegie Publication No. 65, for data). It will be noticed that the graph of the band at 4.5 μ is much steeper (the horizontal scale is different for these bands) than are the ones farther toward the infra-red. The maxima of the absorption bands lie close to the graph drawn through them.

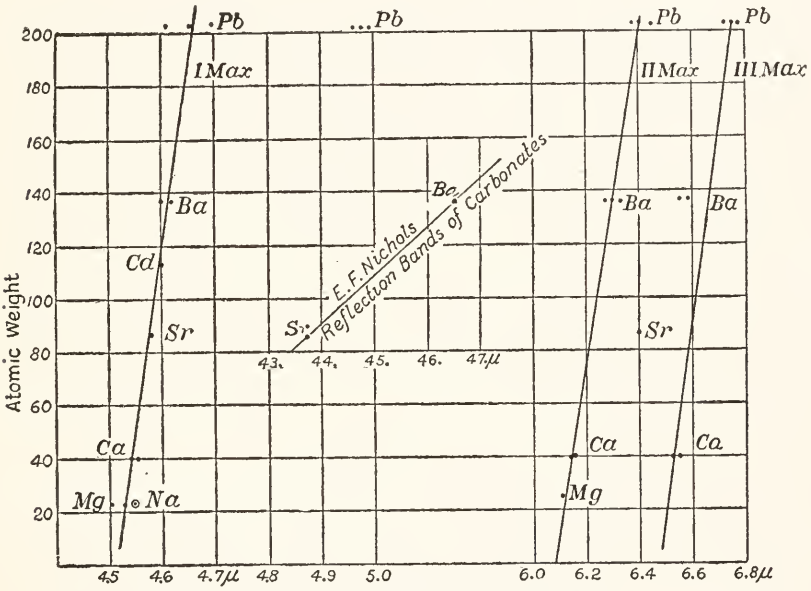

FIG. 45. — Maxima of absorption bands of sulphates.

The second and third maxima of the absorption bands at 6.2 and 6.5 μ are quite close to the graph, except $SrSO_4$, which has but one maximum lying midway between the two graphs. From this it would appear that the $SrSO_4$ band may be the mean of two unresolved bands (see, however, Part V, Chapter III). The slant of these graphs is less than in the preceding one.

For a discussion of the graph at 45 μ see Appendix III.

Considered as a whole, the data presented demonstrate very conclusively the influence of the molecular weight of the basic atom or "ion" upon the position of the maximum. The results explain why the increase in the number of the *groups* of atoms (see carbohydrates) had no effect upon the position of the maximum. This is to be expected if the *cause* of the band is due to the group of atoms; but the *position* of the band

depends upon the metallic (basic) atom to which the group of atoms is united to form a compound.

It is a remarkable fact that nearly all the substances examined, especially the oxides, have a region of strong selective reflection from 8 to 12 μ. Drude[1] has shown that the optical properties (*e.g.*, dispersion) lead to the conclusion that each atom is a union of many independently vibrating elementary masses or ions. In the ultra-violet the absorption band is due to the sympathetic vibration of particles which have a charge and a mass identical with the negative ion or "electron," while in the infra-red the absorption and reflection bands are due to positive ions ("ponderable atoms") which have a mass of the order of magnitude of the atom. From this standpoint, one would expect to find a shift of the maximum toward the long wave-lengths, as we increase the atomic weight of the element which is attached to the radical.

The latest theoretical discussion of this subject is due to Einstein,[2] who shows how the theory of radiation, especially Planck's, leads to a modification of the molecular-kinetic theory of heat, and clears up points heretofore difficult. He also shows relations between the thermal and optical properties of solid bodies.

TABLE II.

Element.	Atomic heat = atomic weight × specific heat.	λ calculated.	Substance.	λ observed.	λ calculated.
		μ		μ	μ
S and P.....	5.4	42	CaFl	24; 31.6	33; >48
Fl.....	5	33	NaCl.....	51.2	>48
O.....	4	21	KCl.....	61.2	>48
Si.....	3.8	20	$CaCO_3$.....	6.7; 11.4; 29.4	12; 21; >48
B.....	2.7	15	SiO_2.....	8.5; 9.0; 20.7	20; 21
H.....	2.3	13			
C.....	1.8	11			

From the value of the atomic heat of a substance, he computes the maxima of the bands of infra-red selective reflection. The observed reflection bands and the same as calculated by Einstein are given in table II. From this table it will be seen that carbon (diamond) would have a large reflection band at 11 μ, which is possible, as will be noticed in the transmission curve, fig. 30.

This table shows that certain calcite maxima are due independently to C at 11.4 μ and to O at 21 μ. In quartz the band at 20 μ is due to Si at 20 μ and O at 21 μ. From this line of reasoning, it would appear that the large reflection band of carborundum at 12.5 μ is due to C, and that there is another band at 20 μ due to Si. A similar computation for selenium and iodine indicates a reflection band at about 42 μ.

[1] Drude: Ann. der Phys. (4), **14**, 677, 1904.

[2] Einstein: Ann. der Phys. (4), **22**, p. 181, 1907.

CHARACTERISTIC BANDS OF QUARTZ AND OF SILICATES.

About half the minerals known are silicates. Their percentage composition has been ascertained by quantitative analysis, but little has been possible, as yet, in establishing their constitutional formulæ. In organic chemistry the constitution of compounds has been determined by vapor density determinations, by the preparation of series of derivatives, by the replacement of certain constituents by organic radicals, or by studying their physical properties in solution. In mineralogy this has, as yet, not been possible, and the constitution of many of the minerals has been derived mainly from analogies with other substances which are better understood. The silicates are sometimes grouped as follows: *disilicates* (RSi_2O_5) are salts of disilicic acid ($H_2Si_2O_5$), and have an oxygen ratio of silicon to bases of 4:1; *polysilicates* ($R_2Si_3O_8$) are salts of polysilicic acid ($H_4Si_3O_8$), with oxygen ratio of 3:1; *metasilicates* ($RSiO_3$) are salts of metasilicic acid (H_2SiO_5), oxygen ratio of 2:1; *orthosilicates* (R_2SiO_4), salts of orthosilicic acid (H_4SiO_4), oxygen ratio of 1:1.

Among the complex silicates, and often among the simple ones, not only is the actual molecular structure in most cases doubtful, but even the simple empirical composition of many species is still unsettled. A single species may vary greatly in composition. This has been explained by regarding the different forms as derivatives of a normal salt in which various atoms or molecular groups may enter. It is not surprising then, in the present limited study of their reflection spectra, to find no very important relations among the reflection bands of silicates.

From previous work it is difficult to decide what one ought to expect in the question of the coincidence of bands in SiO_2 and in silicates. In the case of the carbonates there are no bands (except a small depression at 4.6 μ in common with CO) coincident with those of CO_2; and we might expect a similar condition to obtain in the silicates and SiO_2. On the other hand, in the carbohydrates having a structure indicating CH_2 and CH_3 groups, there is a coincidence of certain characteristic bands with those of ethylene (C_2H_4) and ethane (C_2H_6). The introduction of oxygen atoms, however, modifies the spectrum, and, as a rule, there is no longer a coincidence with the former bands. Furthermore, in SO_2 the maximum at 8.7 μ is in coincidence with a similar band found in many sulphates, while the band at 10.4 μ is in common with a similar one in fuming sulphuric acid and is probably due to SO_4. From this it is difficult to predict what one ought to expect in the case of SiO_2 and of the silicates. From previous observations that groups of chemically-related substances have similar absorption spectra, one would expect to find a similar condition to obtain in the various groups of silicates. The present investigation is not extensive enough to draw general conclusions. Moreover, the constitution of the minerals is in many cases in doubt, so that the lack of similarity in

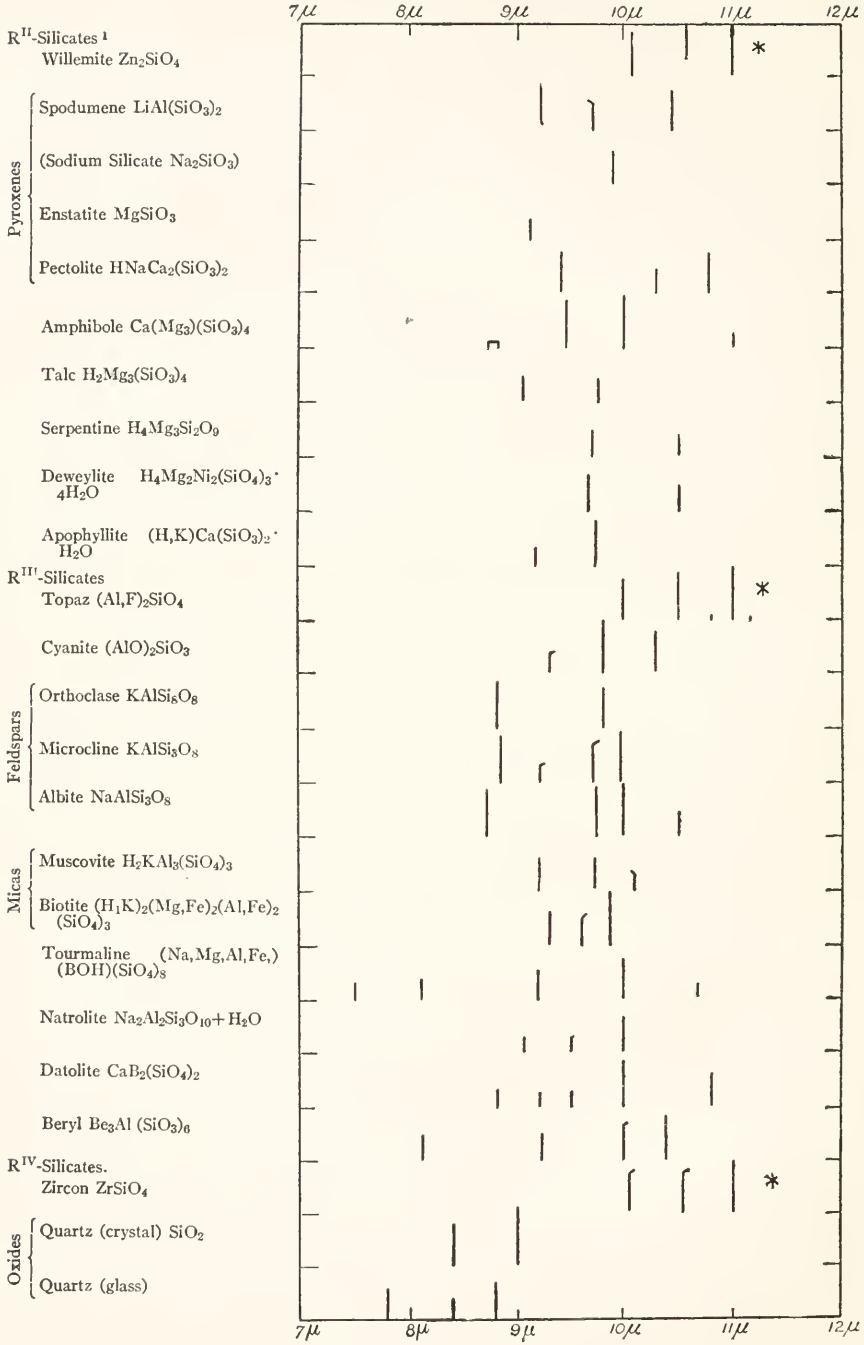

Fig. 46. — Line spectra of silicates.

[1] R^{II}, Valence of metal is indicated by the exponent.

spectra of supposedly related silicates is not due to a fault in the criterion for judging such relations. The reflection bands of the various silicates examined are represented by lines in fig. 46. The lines broken at the top indicate that the reflection bands are not well resolved. The silicates of the divalent metals, R^{II}-silicates, are metasilicates, while the R^{III}-silicates are orthosilicates, as noticed on a previous page. Since there is a band (at 10 μ) in common with both groups we are at liberty to assume that the division into ortho- and meta-silicates is not a characteristic in the spectra. Again, the groups of chemically related minerals may or may not have similar spectra. Thus, the pyroxenes and micas have dissimilar spectra. Serpentine and deweylite (and the feldspars) have similar spectra. Orthoclase and microcline, which are isomeric, show their structure by their dissimilar spectra. The amphibole seems out of place. Spodumene, talc, serpentine, deweylite, apophyllite, microcline, albite, and muscovite have a group of atoms in common, which causes a band at about 9.7 μ. Amphibole, topaz, microcline, albite, tourmaline, natrolite, datolite, and beryl have a group of atoms causing a band at 10 μ.

Serpentine, deweylite, topaz, and albite have a common radical causing a band at 10.5 μ. Quartz glass, datolite, orthoclase, and possibly amphibole, have a band in common at 8.8 μ.

The group of triplets in willemite, topaz, and zircon is unusual, the maxima being, on an average, at 10.1, 10.6, and 11 μ, respectively. In willemite (R^{II}) the bands are sharp and well defined, in topaz (R^{III}) the bands are not so well resolved, while in zircon (R^{IV}) the bands are almost indistinguishable. Whether this change in sharpness of bands is due to the variation in valence is a pertinent question. Previous work indicates that the variation in the sharpness of the bands is due to the amount of oxygen present — oxygen sharpens the bands. In crystalline quartz and

TABLE III.

Compounds having the following groups.	Show characteristic absorption and reflection bands at:						
	μ	μ	μ	μ	μ	μ	μ
CH_2 order CH_3	3.43	6.86	13.6 to 13.8	14			
NH_2	2.96	6.1 to 6.15					
C_6H_6	3.25	6.75	8.68	9.8	11.8	12.95	
NO_2	7.47	9.08?					
OH	2.95	(3.0)					
NCS	4.78						
R–SO_4[1]	4.55	6.1	6.5	8.2	8.7	9.0	9.2
R–SiOx	3	8.4	8.8	9.7	10	10.5	11
R–CO_3[1]	6.5	6.8	11.4	14	29.4		

[1] The position of the maxima in these compounds depends upon the atomic weight of the basic element, R, with which the group or acid radical is combined.

quartz glass there is a band in common at 8.4 μ, showing a common group of atoms. This band, with the five groups in common with the silicates, makes a total of six groups of bands, the radicals which cause them being, as yet, undetermined. These bands are at 8.4, 8.8, 9.7, 10, 10.5, and 11 μ. This seems to substantiate the view expressed in Carnegie Publication No. 65, p. 95, that in the silicates there appear to be several silicon-oxide radicals, one or more of which are present in each mineral, or even in the different specimens of the same mineral.

In table III are given the characteristic maxima of the reflection and absorption bands of radicals studied in this and in previous work.

PART VII.

INFRA-RED EMISSION SPECTRA.

CHAPTER I.

EMISSION SPECTRA OF METALS IN HYDROGEN.

In Carnegie Publication No. 35 the writer presented the results of an examination of the arc spectra of various metals. It was there shown that only the alkali metals have strong emission lines in the infra-red. In the case of metals like copper, iron, and zinc there was a weak continuous spectrum in the region of 2 to 3 μ, which appeared to be due to the hot oxides formed in the arc. If this be true, then one would expect to eliminate this radiation by producing the arc in an atmosphere of hydrogen. During the past year (1907) this work has been repeated, using an arc inclosed in a metal case which was filled with hydrogen. A Rubens thermopile was used to measure the radiation. The galvanometer had a full period of 16 seconds; its sensitiveness was $i = 1.7 \times 10^{-10}$ for a scale at 1 m. When used with the thermopile the temperature sensitiveness was such that a deflection of 1 mm. $= 1 \times 10^{-5}$ ° C. for a scale at 1 m.

The spectrum was produced by means of the rock-salt prism and mirror spectrometer (slits 0.5 mm.) which were described in Carnegie Publication No. 65.

(*a*) NICKEL ARC IN HYDROGEN.

With this outfit the emission spectrum of nickel in hydrogen was examined. The window of the metal case inclosing the arc was of thin glass which absorbed all the radiation beyond 3.5 μ. The metal electrodes were about 1 cm. diameter, with the ends cut wedge-shaped. This produced a long narrow arc, an end-on image of which was projected upon the spectrometer slit by means of a 12 cm. focus, concave mirror.

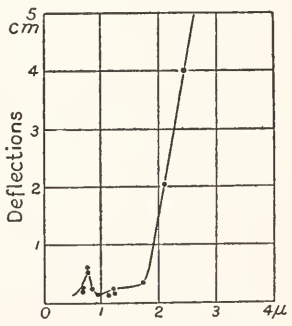

FIG. 47. — Nickel arc in hydrogen.

The spectrum appeared continuous in the red, where the maximum radiation was observed. The results are shown in fig. 47, where a strong emission is to be observed at 0.75 μ. Beyond 2 μ the radiation from the hot electrodes is indicated by the rapid rise in the radiation curve.

The results show but little radiation in the region of 2 μ, where previously a continuous spectrum was observed. It is also to be observed that no strong emission lines occur at 1 μ, where the alkali metals have intense lines.

(*b*) SPARK SPECTRA OF METALS IN HYDROGEN.

For producing a high potential spark (arc) a 10,000-volt transformer, with 100 volts, 1 to 9 amperes in the primary, was used. From one to three glass condenser plates, each having a capacity of 0.0028 M.F., was placed in parallel with the electrodes. This produced a very intense arc. An image of the electrodes was projected upon the spectrometer slit by means of a short focus, concave mirror. The electrodes were about 3 mm. diameter, filed wedge-shaped. They were mounted in glass holders which were fitted into a glass vessel of about 200 c.c. capacity by means of ground joints (designed by Dr. Nutting), which permitted adjustment of the electrodes as shown in fig. 48. The radiation passed through a quartz window about 3 mm. thick, hence opaque beyond 4 μ. The hydrogen was prepared electrolytically in an automatic glass generator shown in fig. 49.

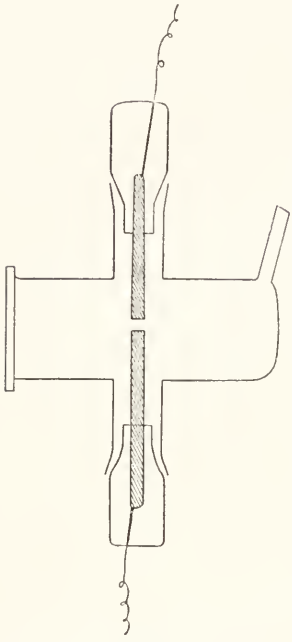

FIG. 48. — Hydrogen spark tube.

The spark (arc) spectra of the following metals were examined: aluminum, copper, and calcium. For electrodes of the latter, thin pieces were sawed from a large bar of the metal, which were then hammered into wires about 2 to 3 mm. in diameter. These were kept under oil to prevent oxidation. The result of the examination was rather disappointing, for no appreciable radiation could be detected up to 3.5 to 4 μ, where the electrodes gave from 3 to 10 cm. deflections. This latter was eliminated by covering the spectrometer slit over the whole length, except about 2 mm., which permitted only the radiation from the high potential arc (spark) to enter the instrument. The fact that no deflections greater than 1 mm. were observed is not due to a lack of sensitiveness of the instrument, and it may be concluded that no emission lines were produced which had an appreciable intensity. This is rather surprising, for calcium is close to the group of elements having emission lines in the infra-red.

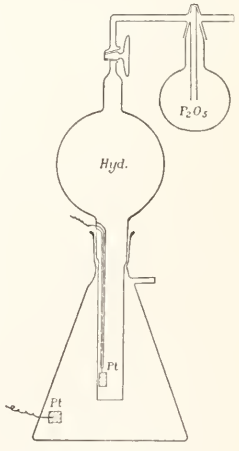

FIG. 49. — Automatic electrolytic hydrogen generator.

EMISSON SPECTRUM OF THE CARBON ARC.

The emission spectrum of carbon was previously examined by the writer in connection with the emission spectra of metals and salts of metals in the carbon arc. It was found that the *violet* part of the carbon arc had several emission lines near 1 μ, followed by a weak continuous spectrum with a maximum at about 2.5 μ. There seemed to be a slight emission band at 4.52 μ, which on subsequent examination could not be reproduced. The writer, therefore, concluded that in the combustion of the carbon electrodes no CO_2 or CO is formed, but that the carbon passes off as a vapor.

Furthermore, it was found that when salts of the alkali metals (Na, K, Li) were present, even in small quantities, there was a strong emission line at 4.52 μ.

The radiometer used was not very sensitive, while the conclusion that the carbon arc was mainly vapor of carbon did not seem satisfactory, hence the work was repeated, using electrodes of ordinary gas carbon and also of pure Acheson graphite. The latter is difficult to burn even when the length of the arc is only 2 mm. long.

In the present examination a Rubens thermopile was used. The galvanometer period was 10 seconds, and its sensitiveness was about 2.5×10^{-10} amperes. The spectrometer slit was 0.1 mm. wide and 2 mm. long, and an image of the blue vapors of the arc was projected upon it by means of a short focus mirror. The carbon electrodes were of the usual diameter, 12 mm., while two sizes (5 and 10 mm. diameter) of graphite electrodes were used. An examination was also made using one carbon and one graphite electrode.

In fig. 50 are given the emission curves of the carbon arc, *a* and *b* for a solid electrode with soft core, using 15 amperes (D. C.), while curve *c* is for hollow electrodes (2 mm. holes). The latter was examined to learn whether the air, drawn in through the hole, had any effect — which appears negative.

In curves *d* and *e* are given the emission curves observed at various times, under various conditions, when the hollow carbons contained the salts of the metals NaCl and KCl. The length of the arc was from 5 to 7 mm. and in some instances was as much as 12 mm. On the whole, whatever the current — from 5 to 15 amperes — there is always an emission band at 4.5 μ when salts of the alkali metals are in the arc, while the pure carbon (on 15 amperes) had little if any selective emission in this region.

An examination was then made of the emission of pure graphite (Acheson's). The direct-current arc was maintained with difficulty and could not be made longer than 4 to 5 mm.

In fig. 51 are given the observed results for the emission of pure graphite

in the region of 4.5 μ. The purity of this material may be judged from the entire absence of the sodium lines; only the violet carbon bands were

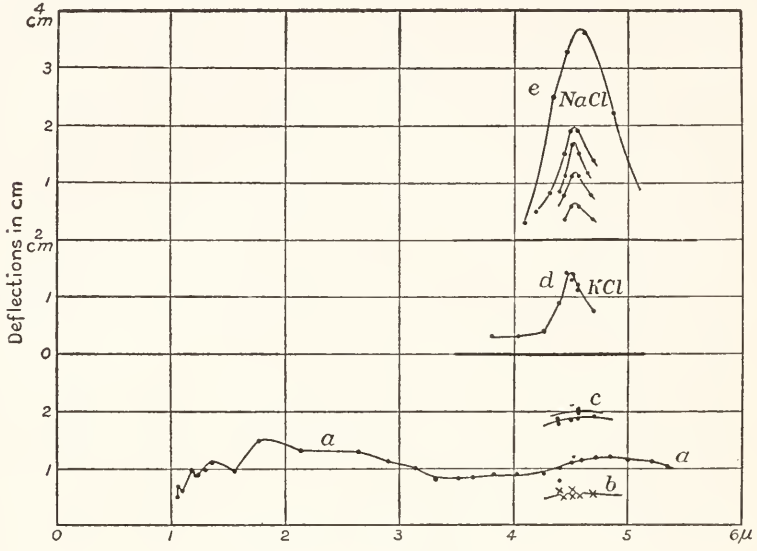

FIG. 50. — Emission of carbon arc.

visible. The lower curves are for a current of 7 amperes (120-volt circuit), while the two upper curves are for a current of 8 amperes, all of

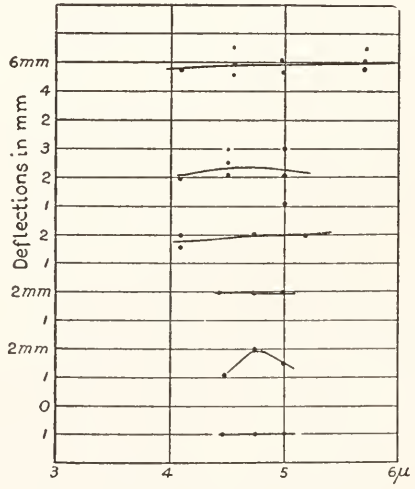

FIG. 51. — Emission of graphite arc (8 amperes).

which were obtained under various conditions. On account of the difficulty in maintaining a steady arc, no attempt was made to map a strong emission band extending from 1.2 to 1.7 μ and a second band extending

from 2 to 3 μ. The latter is the one always observed and generally attributed to oxides, in the case of a metallic arc.

It is to be observed that the deflections are only a few millimeters as compared with the large deflections when salts of metals are present.

An examination was then made of the graphite arc, using a current of 4 amperes. The length of the image of the arc projected upon the spectrometer slit (which was also the length of the arc itself) was only from 2 to 3 mm. The arc was very unsteady and difficult to keep burning. The results are given in fig. 52, curves *a* (4 amperes) and *d*. Curve *a* is for an arc-length of 2 mm., while *d* is for a length of about 5 mm. For the shorter arc the maximum is shifted toward the long wave-lengths.

In this same figure, curve *b* gives the emission when the cold (negative) electrode was a gas carbon (with soft core) and the positive electrode was pure graphite. The current was varied from 5 to 6 amperes, and the length of the arc was from 4 to 5 mm. There is an emission maximum at 4.6 μ, as was found for the two graphite electrodes. For comparison of position and intensity, the emission band of carbon dioxide in a Bunsen burner is given in curve *c*, fig. 52. The results with the pure graphite show that there is a sharp emission band at 4.65 μ (4.55 μ for a longer arc), where previously, for a larger current, there was none. Since all the observations extend over the same range of length of arc, it appears that the occurrence of the emission band depends upon the current and that it disappears for a large current. This is certainly extraordinary. Since the observations on graphite were made in quick succession on the same day, as given here, and since no changes were made in the apparatus, the lack of an emission band for a current of 7 amperes is not to be attributed to a fault in the adjustments. To attribute the occurrence of emission bands, when salts of metals are present, to some "catalytic" action caused by the presence of these metals does not elucidate matters very much.

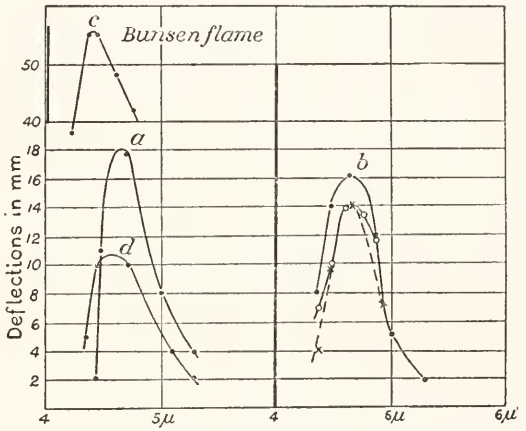

FIG. 52. — Emission of graphite arc (4 to 6 amperes).

Paschen was the first to observe that the emission band of carbon dioxide at 4.3 μ shifts to the long wave-lengths with rise in temperature. At that time the dissociation of carbon dioxide at high temperatures was but little investigated. Since the absorption band of carbon dioxide is at 4.3 μ and that of carbon monoxide is at 4.6 μ, if the emission band is due to a pure thermal effect, then one would expect to find that, with rise in

temperature and the consequent dissociation of CO_2 into CO, the maximum of the emission band of CO_2 will shift toward that of CO. The writer has observed this emission band of CO_2 under various conditions of temperature. In the emission spectrum of the Hefner lamp it was found at 4.36 μ. In the arc spectra of the salts of the metals previously studied it was found at 4.52 μ. In the vacuum-tube radiation of CO and CO_2 the maximum was found at 4.75 μ. In the acetylene flame it was found at 4.4 μ, while in the present examination it occurs at 4.55 to 4.65 μ. It has always appeared to the writer that this shift of the emission maximum with rise in temperature is due to dissociation of CO_2 into CO, and no satisfactory data has yet been found to refute this assumption. The vacuum-tube radiation of CO and CO_2, where the maximum emission occurs at the same place for both gases, seemed to prove the point. The present data furnish further evidence that the cause is due to dissociation. For, using a graphite arc on 4 amperes, when the arc is short, and the hottest, the maximum occurs at 4.65 μ. When the salts of the metals are introduced into the arc they are ionized and the metals carry the greater part of the current. The resistance is reduced, and hence the temperature (and dissociation of CO_2) is reduced. Here the maximum is at a shorter wave-length corresponding to less dissociation of CO_2. While this explains certain points it fails to account for the lack of an emission band when the current is large, 8 to 15 amperes. It is hardly permissible to assume that neither CO or CO_2 is formed at this high temperature and that the electrode disappears in the form of vapor, though the writer made this assumption at the conclusion of his previous examination of the carbon arc.

The change in density of the gases in the two cases will not account for the observations, for even the smallest amount of CO and CO_2 is capable of emitting perceptible radiation, as was found in the experiments with the vacuum tube. As a whole, the mechanism producing this radiation is not understood and further experiments will be needed to gain insight into this subject.

THE INVESTIGATIONS OF MOLL.

While the above experiments on the carbon arc were being concluded the investigations of Moll[1] on infra-red metallic spectra appeared in print. He examined the emission spectra of the salts of the metals of Na, K, Rb, and Cs in the carbon arc, using for the purpose a rock-salt prism, a thermopile, and an automatic device for recording the galvanometer deflections. The apparatus was a little more sensitive than the radiometer previously used by the writer, while his dispersion was almost twice as great, and with the automatic device he was able to explore the region beyond 2 μ more thoroughly than was possible by making personal observations. In

[1] Moll: Onderzoek van Ultra-Roode Spectra, by W. J. H. Moll. Dissertation, Utrecht, 1907; Proc. Amsterdam Acad., Feb. 21, 1907.

the region from 2 to 4 μ he succeeded in resolving the emission into separate bands, which the writer, from the smallness of the deflections and the limited number of observations, recorded as a continuous spectrum. He found the CO_2 band at 4.44 μ when he used the salts in the arc, and also for various kinds of carbon electrodes. His energy curves for sodium and for potassium are given in figs. 53 and 54, respectively, in which the resolution of the energy in the region of 1.5 to 4 μ into separate bands is well illustrated. The automatic apparatus succeeded in doing what physical

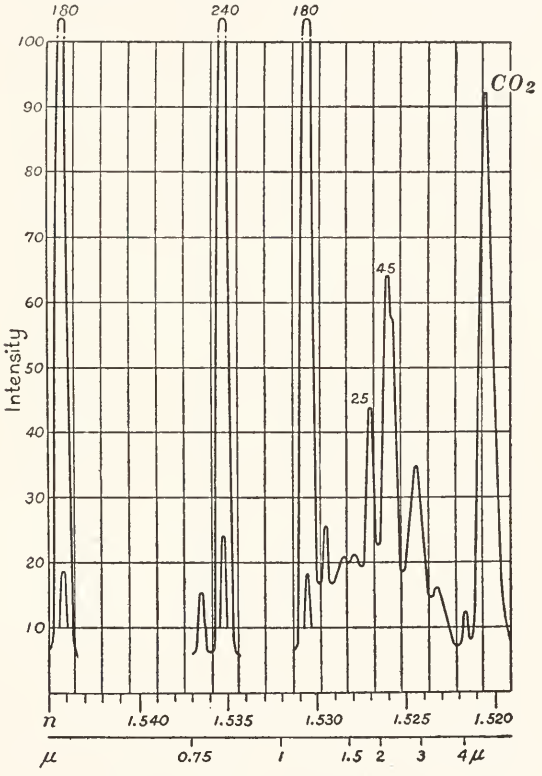

FIG. 53. — Emission of sodium (Moll).

endurance would hardly permit, in mapping this region. No curves are published for the carbon electrodes, but considerable comment is made on the fact that in every case he observed an emission band of CO_2, while the present writer did not find the band, except when using salts in the arc. From the aforesaid observations on the radiation from graphite, it is evident that the conditions were different in the two cases. The writer had observed the same phenomena as did Moll, who, in his comments, missed the point emphasized by me, viz, that whether or not the spectrum at 2 to 4 μ is a complex of small emission bands, the emission bands of the alkali metals at 0.76 to 1 μ are the most intense in the whole spec-

trum, indicating a much higher temperature (if the radiation is purely thermal) than would be the case if the emission bands at 2 to 4 μ were the more intense.

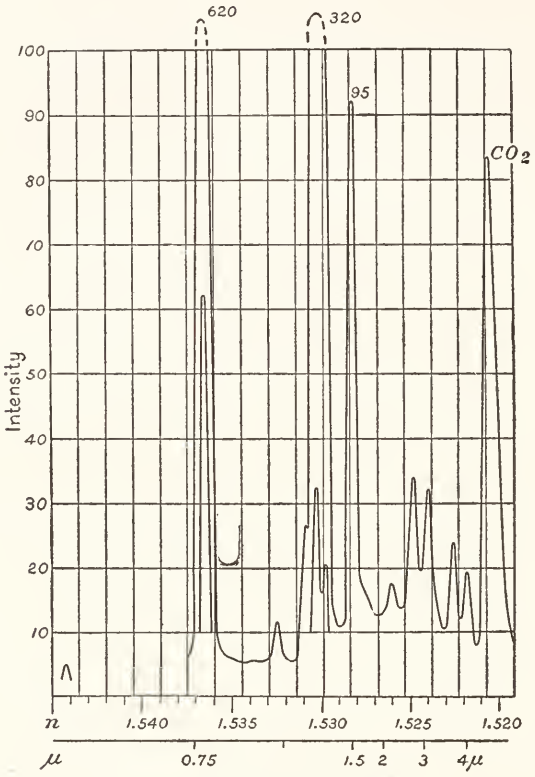

FIG. 54. — Emission of potassium (Moll).

RADIATION AT ROOM TEMPERATURE.

The distribution of energy in the spectrum of a complete radiator has been determined for temperatures varying from 373° to 1800° abs., and the constant in the "displacement law" $\lambda_{max}\ T = A$ has been found to be 2930 (2940, Lummer and Pringsheim; 2920, Paschen). For bright platinum the value of this constant is about 2630. The measurements of Lummer and Kurlbaum[1] show that at low temperatures (492° abs.) the emissivity of iron oxide is 0.3, while bright platinum is only about 0.04 that of a complete radiator at the same temperature. The spectral distribution of radiation at low temperatures has been given but little attention. This is due in part to the impracticability of reducing the temperature of the radiation meter below that of the room. The problem is therefore reversed, in that the radiation meter (bolometer, radiometer, or thermopile)

[1] Lummer & Kurlbaum: Verb. Phys. Ges. Berlin, **17**, p. 110, 1898.

is allowed to radiate to what is generally the source, which is at a much lower temperature. The first examination was made by Langley:[1]

He located the maximum galvanometer deflection in the region of 8 μ, but adds that the position of "the maximum depends upon a single observation of some delicacy, which is liable to subsequent correction." He further adds that for this temperature difference of $-18°$ the maximum ought to be at 10 to 11 μ. This would indicate that there was some confusion of ideas as to what was really taking place. The energy emitted by the vessel of ice and salt is very small in comparison to the amount it absorbed from the bolometer. Hence the galvanometer deflections are a measure of the radiation emitted by the bolometer to the vessel of snow and ice, and the observed maximum is for a temperature of $-2°$ instead of $-18°$ C. However, since a bolometer strip is always at a higher temperature than the surrounding atmosphere, it is quite probable that, although the observations were made during zero weather, the maximum observed is really due to a higher temperature of the source (bolometer strip) than $-2°$ C. In fact, from the "displacement law," which was then unknown, and from our present knowledge of radiation of different surfaces, it is quite possible that the temperature of the bolometer was as high as 20 to 30° C.

Mendenhall and Saunders[2] state that they found the energy curve of a complete radiator at $-90°$ C. From their discussion of the energy curve of a body at the temperature of boiling liquid air where the emission maximum should lie at 30 μ (which, of course, is possible if one could reduce the temperature of the radiometer below this point in order to make measurements), it would appear that they, too, had not considered their radiation curve to be due to the bolometer strip. Moreover, the use of a bolometer to deduce a distribution of energy curve at low temperatures, where the bolometer itself becomes the source, is not very satisfactory, due to the fact that the temperature of the radiating strip can not be determined.

Lummer and Pringsheim[3] obtained a small portion of the spectrum energy curve of a screen at room temperature, which they used during their radiation experiments. The first really lucid discussion of the subject is due to Stewart,[4] who found the spectrum energy curve of a Nichols radiometer radiating to a receiver at liquid-air temperature. The maximum deflections observed were 4 mm. The temperature of the room (and radiometer vane) was 24° C. or 297° abs. The observed maximum

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[1] Langley: Amer. Jour. Sci., **31**, p. 1, 1886. "The radiator was the bolometer itself at a temperature of $-2°$ C., and the source radiated to was a vessel of snow and salt at $-20°$ C., thus determining the distribution of energy in the spectrum of a surface below the freezing-point of water."

[2] Mendenhall & Saunders: Astrophys. Jour., **13**, p. 25, 1901.

[3] Lummer & Pringsheim: Verb. Phys. Ges., **2**, p. 163, 1900.

[4] Stewart: Phys. Rev., **17**, p. 476, 1903. (In this paper figs. 4 and 6 are interchanged.)

of his energy curve, corrected for slit-width, occurs at 9.2 μ, while the value computed from the "displacement law," using the temperature 297° abs. and $A = 2920$, would be found at 9.8 μ. If we compute the value of this constant from the observed values of λ_{max} and T, then $A = 2722$, which is about 6 per cent lower than for a complete radiator. From experiments on the radiation from plane surfaces, such as a radiometer vane, this departure from the radiation of a full radiator is to be expected. Then, too, this form of radiation is complicated by the window before the radiometer vane. In general, the intervening material between the source and the receiver would have no effect. For very delicate radiometers, however, the writer found (Carnegie Publication No. 35) that the inequality in the radiation from the radiometer window had a great effect upon the position of the vanes. Just how much this would affect the vane in the present case is unknown. In the present investigation a Rubens thermopile (20 junctions of iron-constantan) was allowed to radiate to a copper vessel at liquid-air temperature. A mirror spectrometer and rock-salt prism, described in Carnegie Publication No. 65, were employed to produce the energy spectrum. The only changes introduced consisted in replacing the Nernst heater by a short focus mirror, which projected an image of the bottom of the vessel at liquid-air temperature, upon the spectrometer slit. The galvanometer used with the thermopile had a sensitiveness of $i = 2 \times 10^{-10}$ amperes and a full period of about 12 seconds. The deflections were very unsteady, due to air currents caused by the evaporation of liquid air. The thermopile was placed in the position formerly occupied by the radiometer and was covered by the inner metal shield, with a slit 1 by 15 mm. area. The whole was inclosed in a metal tube covered with felt. This formed a more perfect black body than is possible with a radiometer. The receiver to which the thermopile radiated consisted of a thin cylindrical copper vessel about 4 cm. diameter and 12 cm. long (covered on the inside with copper oxide and lampblack), which was suspended in a vessel of liquid air, as shown in fig. 55. The receiver was kept stationary and

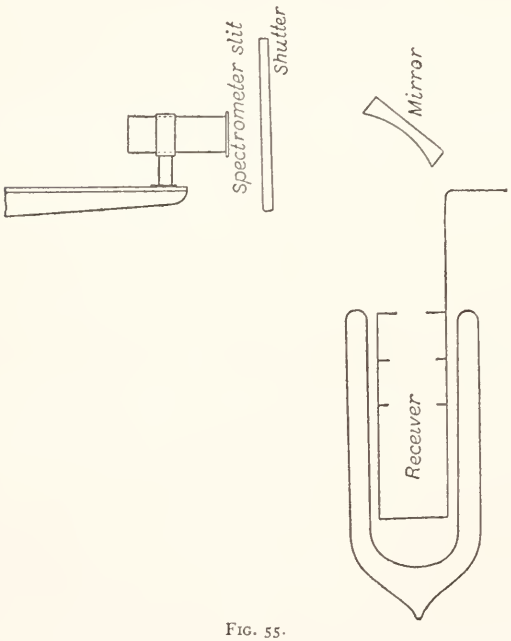

FIG. 55.

the height of the vessel of liquid air was regulated. The temperature changed so rapidly that it was necessary to begin taking readings with the liquid air just touching the bottom of the vessel, when fairly consistent results were obtained. The observations are plotted in fig. 56. Curve *a* is plotted through the mean values of the observations, while curve *b* is drawn through the highest observed values. The two curves are fairly consistent, considering the difficulties in making the observations. In the region of 6 μ atmospheric absorption reduced the deflections.

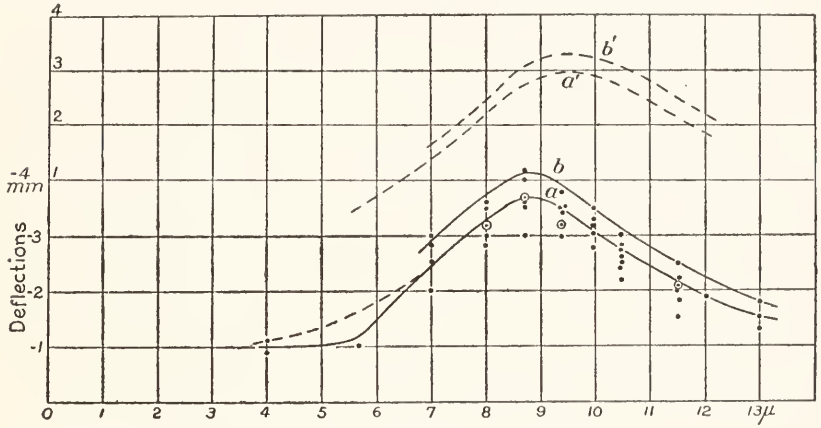

FIG. 56. — Emission spectrum of Rubens thermopile.

Curves *a'* and *b'* are the two lower curves after correcting for variation in slit-width, *i.e.*, reducing them to a normal spectrum. The maximum of these radiation curves lies at about 9.6 μ. The temperature of the thermopile was 21° C., or 294° abs. Substituting these values in the "displacement" formula, the constant is $A = 2822$, which is about 3 per cent smaller than that of a complete radiator. For the latter, the maximum would occur at about 9.95 μ. It appears that the thermopile approaches very closely to that of a Kirchhoff radiator.

SELECTIVE RADIATION FROM THE NERNST GLOWER.[1]

The study of the radiation from metal filaments of incandescent lamps is of interest in connection with the speculations as to whether the great light emissivity (high luminous efficiency) is due to an abnormal emission in the visible spectrum, with a corresponding suppression of the radiation in the infra-red, or whether the effect is due to the high temperature at which the lamp is burning. In the latter case, the distribution of energy in the spectrum may be uniform (no discontinuities), but a great deal of it will lie in the visible spectrum. From a theoretical consideration[2] of

[1] A detailed description of this investigation is given in the Bulletin of the Bureau of Standards, vol. **4**, p. 533, 1908.

[2] Aschkinass, Ann. der Phys. (4), **17**, p. 960, 1905; Einstein, Ann. der Phys. (4), **17**, p. 132, 1905; **22**, pp. 191, 569, 800, 1907.

the fact, that the filaments are metallic, electrical conductors with a high reflecting power in the visible, and probably reflect uniformly high in the infra-red, one would expect the distribution of energy in the spectrum to follow a law similar to that of platinum, but with different constants. The results thus far obtained from a study of such metals as tungsten and osmium support this hypothesis. On the other hand, in the case of oxides, which conduct electrolytically at high temperatures, there is no data to form even a working hypothesis. All the oxides thus far examined have no strong absorption bands near the visible spectrum; the only exception being the oxides of the rare earths, such as cerium, thorium, lanthanum, didymium, erbium, etc., the compounds of which have strong, sharply defined absorption bands in the visible, and at least some of these have absorption bands in the infra-red. It seems to be a characteristic of the oxides, that they have a low reflecting power (like transparent media, electrical non-conductors) throughout the infra-red to about 8 μ beyond which point they have strong bands of metallic reflection. In this region of metallic reflection, the emission will be suppressed[1] in proportion to the reflecting power. In the rest of the spectrum, the emission will be proportional to the absorbing power (general absorption), while at the point where there is a band of selective absorption in the transmission spectrum, there will be an emission band in the emission spectrum, provided the radiation is a purely thermal one, following Kirchhoff's Law.

In the case of the Auer mantle the emission spectrum[2] is a series of emission bands at 1 to 2 μ, with practically no emission in the region from 4 to 7 μ, while beyond 9 μ the spectrum is continuous, and is apparently as intense as that of a complete radiator at the same temperature.

In the case of the Nernst glower, which is a combination of the oxides of cerium, thorium, and zirconium, belonging to the "rare earths," the compounds of which are noted for their strong absorption bands, one would expect the emission spectrum to show strong, sharp emission bands; at least one would hardly expect the emission to follow the same general law of spectrum energy distribution as is known for metals. This, however, has been done in the past, notably by Lummer and Pringsheim,[3] and by Mendenhall and Ingersoll.[4]

The first two investigators, from a rather cursory examination of the Nernst filament, under normal power consumption, found a smooth continuous curve, with a maximum at wave-length $\lambda_{max} = 1.2\ \mu$. From this and from the Wien displacement law, $\lambda_{max}\ T = \text{const.}$ (const. = 2940 for "black body," = 2630 for platinum), assuming that the Nernst glower

[1] Aschkinass, Verh. J. Phys. Ges., **17**, p. 101, 1898. Rosenthal, Ann. der Phys. (3), **68**, p. 791, 1899.

[2] Rubens: Phys. Zeit., **6**, p. 790, 1905.

[3] Lummer & Pringsheim: Verh. Deutsch. Phys. Gesell., **3**, p. 36, 1901.

[4] Mendenhall & Ingersoll: Phys. Rev., **24**, p. 230, 1907; **25**, p. 1, 1907.

belongs to the same class of radiators as platinum and a "black body," they computed $\lambda_{max} = 2450°$ abs., and $\lambda_{min} = 2200°$ abs.

Their computed energy curve of a "black body" having its maximum emission at 1.2 μ departs considerably from the observed curve. Mendenhall and Ingersoll compared the emission of the Nernst glower in terms of a constant comparison lamp, at a certain wave-length in the visible spectrum, at the melting points of gold and of platinum. From this they extrapolated on a straight line assuming that Wien's equation holds for the glower, and found the temperature at normal or any desired power consumption. This leads to erroneous values (which are probably too high, as will be shown presently), due to the fact that the spectrum is the composite of numerous emission bands, which rapidly increase in intensity, in the short wave-lengths, with rise in temperature. They found the normal temperature to be 2300° abs., disagreeing with a recent determination by Hartman,[1] who, by means of thermocouples of different thickness placed against the glower, correcting for heat conduction by extrapolating to a temperature corresponding to an infinitely thin couple, found the temperature to be 1800 abs. Although this method had previously been extensively used, with fair success, in measuring temperature of gas-flames, it is not suited to the glower, in which there is no layer of hot gas to even partially compensate for the heat lost by conduction.

That the Nernst glower emits selectively in the visible spectrum, has been shown by Kurlbaum and Schulze,[2] who found a minimum of emission at 0.52 μ, which became fainter with rise in temperature, and disappeared entirely at high temperatures.

To this brief review of what has been done on the Nernst glower may be added a paper by its inventor,[3] who showed that the conductivity is electrolytic, while Kaufmann[4] showed that in spite of the entirely different inner mechanism of conduction of a gas in a vacuum-tube, and in a Nernst glower, the electrodynamic phenomena are nevertheless very similar.

The present investigation of the Nernst glower consists in mapping the distribution of energy in the spectrum, varying the power consumption, and hence the temperature.

The apparatus used in this work consisted of the mirror spectrometer,[5] used in the preceding experiments, a perfectly clear fluorite prism, having an angle of 60° and circular faces 33 mm. in diameter, and a bolometer[6] with a hemispherical reflecting mirror. The bolometer strip and spectrometer slit were 0.6 mm. wide, or about 4′ of arc. The upper part of the

[1] Hartman: Phys. Rev., **17**, p. 65, 1903.

[2] Kurlbaum & Schulze: Verh. Phys. Gesell., **5**, p. 428, 1903.

[3] Nernst: Zeit. für Electrochemie. **6**, p. 41, 1899.

[4] Kaufmann: Ann. der Phys. (4), **2**, p. 158, 1900; **5**, p. 757, 1901.

[5] For adjustments see "Investigations of Infra-red Spectra," Carnegie Institution of Washington Publication No. 35, 1905.

[6] Described in this volume, Appendix II.

spectrometer, containing the collimating mirrors, and the Wadsworth mirror-prism outfit, were entirely inclosed by a thin sheet-metal box, lined with black velvet. The spectrometer slit was covered with a clear plate of fluorite. The openings in the top, for adjusting the mirrors, were closed with soft wax, while the hole admitting the axis for rotating the mirror-prism table was tightened with a nut and packing.

Within the box, and below the level of the mirrors, were placed vessels containing phosphorous pentoxide and sticks of potassium hydroxide, which entirely eliminated the absorption bands of CO_2, and water-vapor from the emission curves. A water-cooled shutter was placed before the spectrometer slit, and the Nernst glower, inclosed in an asbestos case to prevent air-currents, was placed close to the shutter. Observations were also made without inclosing the glower, to prove that the effects observed are not due to stray radiation from the asbestos case. In spite of all that has been written about bolometers, it may be added that there was no "drift," unless a poor storage battery was accidentally used.

The auxiliary galvanometer of 5.3 ohms resistance, with a single swing of 4 to 5 seconds, had a current sensibility of $i = 1.6$ to 1.5×10^{-10} ampere. A greater sensitiveness for the same period would have been possible, by using a lighter suspension. The present suspension of ten needles was just heavy enough so as not to be affected by tremors.

Using a battery current of 0.04 ampere the computed temperature sensibility was $5^\circ \times 10^{-5}$ C., which was generally far in excess of that required. The deflections were reduced to 14 to 15 cm., by inserting resistance in series with the galvanometer. The individual readings would vary by 1 mm. or less than 1 per cent, which is as close as the nature of the work required, since the actual deflections were as high as 2000 cm. Furthermore, at high temperatures (especially when operated above normal power consumption) the filament would deteriorate in emission by that amount during the series of observations.

The calibration curve of the fluorite prism was constructed from the refractive indices, found by Paschen,[1] which, after plotting all the observations made by different observers, seems to be as close to the most probable values as observations will permit. Unfortunately the dispersion curve passes through a double curvature at 1.5 μ, just where the energy spectra have their maximum. In the region of 1.5 μ, the correction for purity, so-called "slit-width" correction, is a maximum.

The wave-lengths in the calibration curve were plotted to the fourth decimal place, so that there is a certainty of the values to at least the second decimal place. This, however, is of less importance than the value of the slit-width correction, which was made according to Paschen,[2] the values being obtained from a curve plotted on a large scale to insure

[1] Paschen: Ann. der Phys. (4), 4, p. 299, 1901.

[2] Paschen: Ann. der Phys. (3), 60, p. 714, 1897.

an accuracy greater than required in the work. In a few cases a correction was made for the reflecting power of the silver mirrors, but it was found negligible except in the visible spectrum.

With this apparatus, a series of energy curves was obtained, varying the power-consumption from 16 watts (the lowest at which the glower would conduct on 110 volts) to 123 watts, which is far above the normal. The energy curves, which were continuous, underwent great variations in appearance with rise in temperature. At 2.5 and 3.5 μ depressions would generally appear in the curves, which could not be attributed to experimental errors, and since previous work by others seemed to show that the spectrum is continuous, an attempt was made to locate the disagreement in the apparatus (in the calibration, or in the slit-width correction curve), but nothing would account for it until the filament was run on a 2000-volt transformer which permitted the heating of the glower at a very low power-consumption. At the lowest temperature the glower was a grayish red. The results are given in fig. 57 (110-volt A. C. glower No. 118), and are entirely different from anything hitherto recorded in the emission of solids in the infra-red. At the lowest temperatures (800° to 900° C.) the bands in the region of long wave-lengths are the most intense. As the temperature increases, the bands in the region of 2.5 μ increase very rapidly in intensity, so that by the time the temperature has increased to 1000 to 1100° the intensity of the group of bands at 2 μ is far in excess of those at 5.5 μ.

The depression at 3 to 3.5 μ is to be noticed, for it persists even at normal power-consumption. The region at 2.5 μ is also to be noticed, for the curves at higher temperatures often show a slight depression, not attributable to experimental errors. As the temperature rises (curve *e*, fig. 57) new emission bands appear, notably at 2.5 and 4 μ. This shift of the maximum of intensity of the bands, with increase in temperature, is to be expected, if the emission is a purely thermal one, following Kirchhoff's law, and is the most conspicuous illustration yet recorded.

In fig. 58 are given the emission curves for the glower (200 volts, serial No. 118) at 19.6 and 102.5 watts, respectively. It is to be noticed that the emission curve has already become smooth and continuous, with but two maxima, at 1.4 and 5.5 μ, respectively. In this figure curve *b* is one-tenth the scale of curve *a*.

On the whole, from whatever point of view we consider the data at hand, it is evident that even after the emission spectrum has become apparently continuous it does not follow so simple a law as has been established for solids emitting continuous spectra. It is also evident that any estimation of the temperature of the glower based on these laws will lead to erroneous results. From a commercial point of view the efficiency of such a radiator, in which the emissivity is abnormally high at 0.6 to 0.7 μ, while the maximum at 1.2 μ is abnormally low, must be much higher than that of some

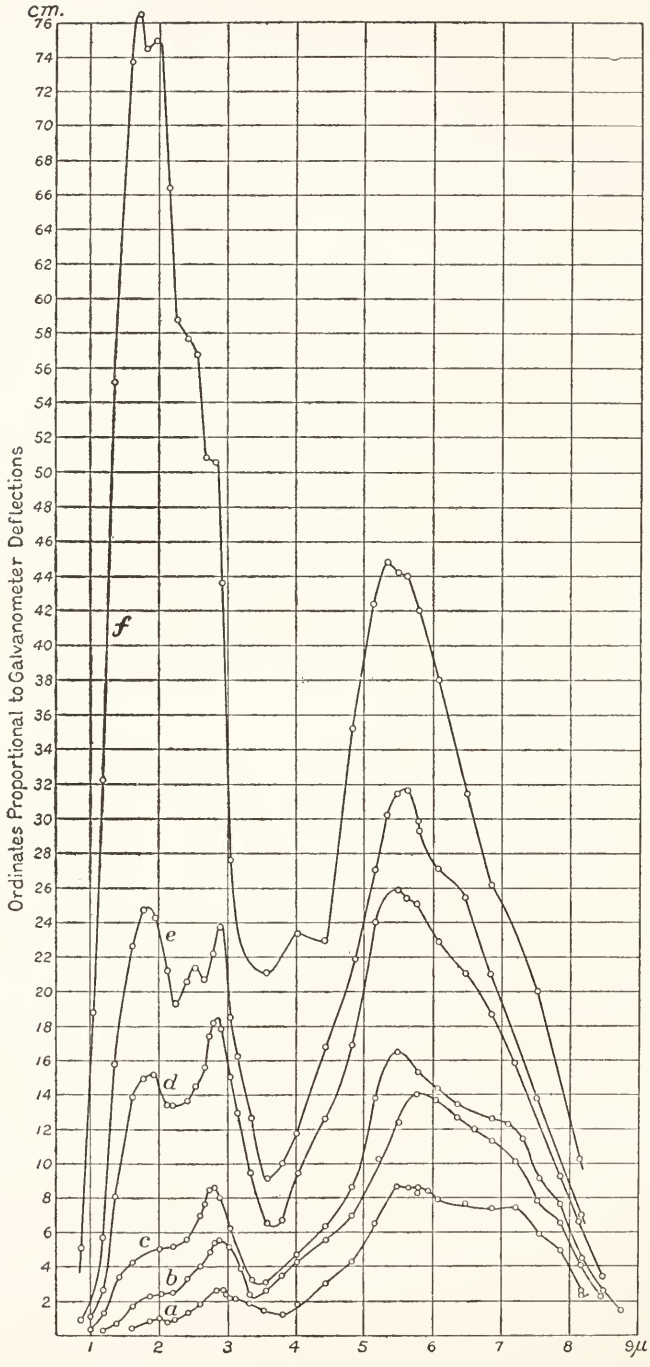

FIG. 57. — Emission spectrum of Nernst glower. $a = 2$, $b = 3$, $c = 4.2$, $d = 6.2$, $e = 7.1$, and $f = 10.6$ watts, respectively.

substance having a radiation law similar to platinum, in which case, in order to attain a similar intensity in the visible, the maximum at 1.2 μ rises to extremely high values.

The results obtained are for filaments made from different lots of material, the 220-volt glower being at least 5 years old. The observations have been made at different dates, on different filaments, all in duplicate, some quadruplicate, and there is reason for feeling that what has

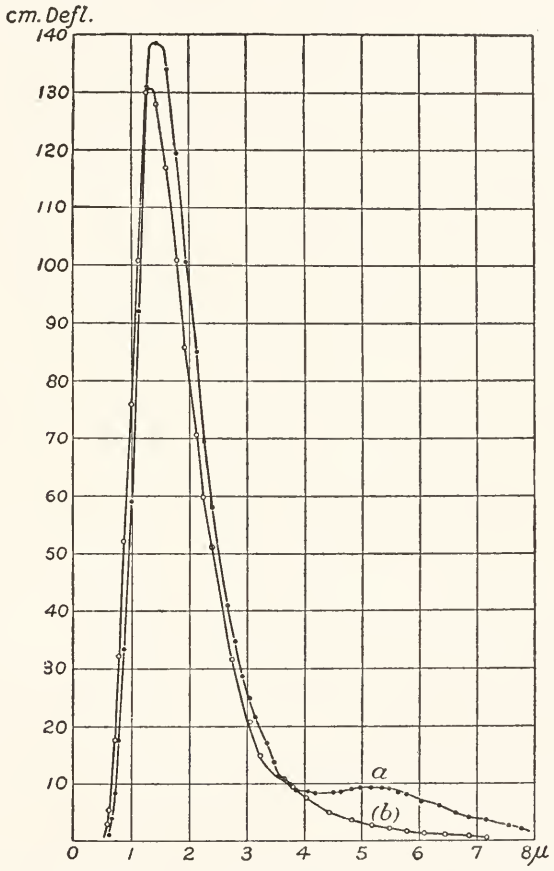

FIG. 58. — Emission spectrum of Nernst glower; (*a*) = 19.6 watts, (*b*) = 102.5 watts; λ_{max} = 1.45 μ and 1.32 μ, respectively.

been observed is a reality. No doubt on examination of other makes of filaments, there will be found a variation in the finer details of the emission bands, at low temperatures, but the gross results can hardly be modified without employing a much larger dispersion and a much narrower bolometer. Some of these bands coincide with certain ones found in the emission spectrum of the Nernst "heater," the results of which are given in Carnegie Publication No. 35.

RADIATION FROM METAL FILAMENTS.

The measurement of very high temperatures is based upon an extrapolation of the laws governing the energy emitted by a body with change in temperature. Our knowledge of these laws is confined to the radiation from platinum and from a uniformly heated cavity (so-called black body) which is the nearest approach to a complete radiator. The remarkable progress made in the development of processes requiring an accurate knowledge of the temperatures involved makes it imperative to study the laws of radiation of various substances with variation in temperature. The object of this and of subsequent investigations is to gain an insight into these laws. In order to determine these radiation laws it is generally necessary to study the spectrum energy curves, using for the purpose a prism that is transparent to heat rays, and some sort of very sensitive heat-measuring device, such as, for example, a bolometer or a thermopile. It is also possible to study the total radiation emitted. The chief difficulty in studying these so-called radiation constants of substances lies in the impossibility of determining the temperature of the radiating surface.

The curves showing the distribution of energy in the normal spectrum of all solid bodies thus far studied are unsymmetrical with respect to the maximum, having the appearance of the probability function, modified by suitable constants. The solids heretofore studied, *e.g.*, platinum, in which it was possible to determine the approximate temperature, have spectrum energy curves, which are represented fairly well by the function,

$$E = c_1 \lambda^{-a} e^{-c_2/\lambda T} \tag{1}$$

In the case of a complete radiator,[1] or so-called "black body," the exponent $a=5$, while for platinum, $a=6$.

In order to determine the constants of the above equation from the spectrum energy curves, it is necessary to know the temperature of the radiator. Fortunately the index a may also be obtained from the spectrum energy curve in which the temperature T is constant (E=galvanometer deflections, λ=wave-length, are variable), without knowing the actual temperature, for it can be shown from equation (1) that the ratio of the emissivities (the observed bolometer-galvanometer deflections) for any two wave-lengths, λ and λ_{max}, is:

$$\frac{E}{E_{max}} = \left\{ \frac{\lambda_{max}}{\lambda} e^{\frac{\lambda - \lambda_{max}}{\lambda}} \right\}^a \tag{2}$$

from which the value of a may be obtained. It was found by Paschen

[1] Paschen: Ann. der Phys. (3), vol. 58, p. 455; vol. 60, p. 663, 1897; (4), vol. 4, p. 277, 1901. Lummer & Pringsheim: Verh. deutsche phys. Gesell., 1, p. 215, 1899.

that for carbon, platinum, etc., the value of a was in agreement with that obtained from a knowledge of the temperature of the radiator.

With this equation it is possible to obtain some idea of the probable total emissivity of a radiating body, as to whether it is proportional to the 4th power ($a-1=4$ for a black body, $a-1=5$ for platinum), or to some higher power of the absolute temperature. Of course the assumption is made that the emissivity function is similar to that of platinum and of a black body. The appearance of the energy curves for various temperatures will give some clue as to the admissibility of this assumption, which is nothing more than has been made by previous observers. How far this assumption falls short of the observed facts, may be seen in figs. 57 and 58 for the Nernst glower, which has a spectrum composed of numerous emission bands. With substances whose energy spectra undergo no change in contour with change in temperature, it does not seem unreasonable to apply our knowledge gained from the behavior of platinum under similar conditions, especially since the filaments are metals, electrical conductors, which, theoretically,[1] should have similar emissive properties. That the

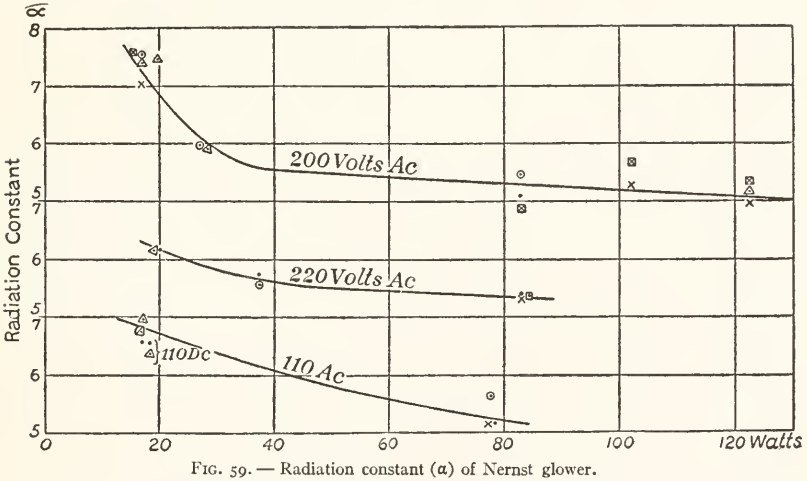

FIG. 59. — Radiation constant (a) of Nernst glower.

method is open to criticism is admitted, but until a better one is suggested, the present method is the only one available without a knowledge of the temperature of the radiator. The apparatus used in this work consisted of a mirror spectrometer, a fluorite prism, and a bolometer, mentioned in the description of the results on the Nernst glower.

The variation of the radiation constant a for the Nernst glower with rise in temperature is shown in fig. 59, from which it will be seen that it decreases from a value of 7 at 18 watts to 5.3 at 80 to 120 watts. These values are taken from the smooth energy curves, such as those shown in

[1] Aschkinass: Ann. der Phys. (4), **17**, p. 960, 1905. Einstein: Ann. der Phys. (4), **17**, p. 132, 1905; **22**, pp. 191, 569, 800, 1907.

fig. 58. The curve for 102 watts was irregular in outline and the values of a obtained at different wave-lengths (indicated by crosses, circles, dots, squares, etc.) undergo great variations. On the whole, it is evident that it is hardly permissible to obtain this constant on the assumption that the radiation law of the Nernst glower is similar to that of platinum or of a complete radiator. The energy curve of a complete radiator having a maximum emission at 1.45 μ falls far below the Nernst glower curve (a, fig. 58) at 5.5 μ, which shows that the emission at 1.45 μ is not as intense as it should be if the emissivity were similar to a complete radiator. For the same reason, the spectral energy curve of a complete radiator having a maximum at 1.32 μ lies far above the glower curve (b, fig. 58) at 5.5 μ.

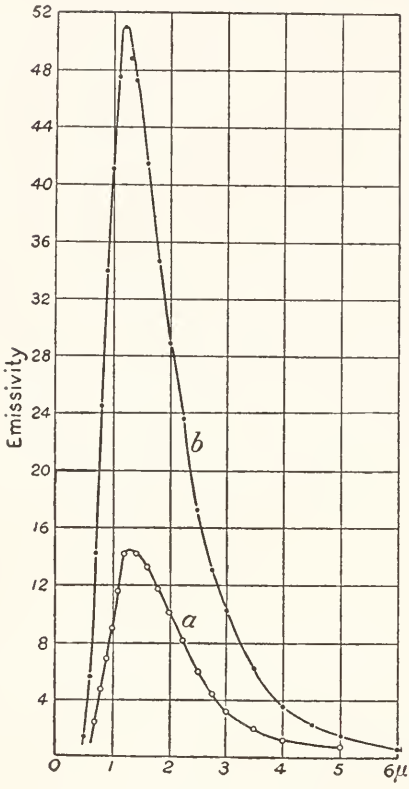

Fig. 60. — Radiation from osmium.

In fig. 60 is shown a series of energy curves of an incandescent filament (3 cm. long) of osmium, when on an energy consumption of curve $a = 2.44$ and curve $b = 7.38$ watts, respectively. The corresponding temperatures, observed with an optical pyrometer, using red absorption glass, are 1607° and 2000° $K._{66\lambda}$ C., respectively, while the computed temperatures, on the assumption that the radiation constants are the same as for platinum (for $\lambda = 1.35$ and 1.2 μ), are 1670° C. and 1907° C., respectively.

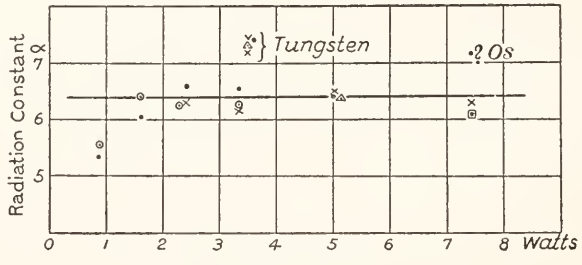

Fig. 61. — Radiation constant (α) of osmium.

These filaments were in glass bulbs similar to that of an incandescent lamp, and had short side tubes with fluorite windows. Fig. 61 shows the value of a of osmium (of fig. 60) for variation in energy consumption.

Except for the lowest temperatures the value of a obtained by this method is about 6.4. The surface became roughened, which lowers the value of this "constant." The weakness of this method lies in the difficulty of obtaining the values of the emissivities, particularly the maximum of the energy curve. Since the filaments are so narrow that the prism-face is only partly covered, the height of the ordinates will depend upon the cone of energy falling upon the prism face. For this reason the energy curves of the different substances can not be compared. The value of a for a short tungsten filament (see fig. 61) was found to be 7.3 for one energy curve. Further experiments on another filament gave a value of $a=6.88$ for the mean of 18 computations and 5 energy curves. The values of a for an untreated carbon filament, for various values of energy consumption, are plotted in fig. 62. As with osmium, the temperature was raised from a

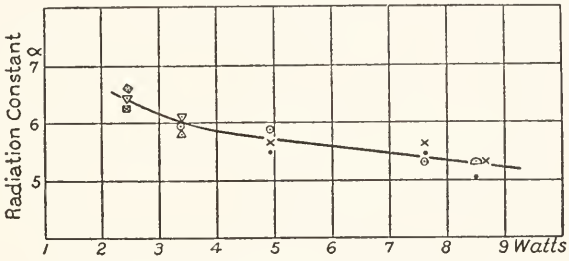

FIG. 62. — Radiation constant (a) of untreated carbon filament.

low red to the normal condition. Apparently the emissivity constant, a, drops from 6.4 at about 900° to 5.3 at 1800° to 2000° C. Paschen found no such variation for the specimens of carbon examined. Neither did he find a variation in a for the oxides of copper and of iron. On the other hand, Lummer and Kurlbaum, by measuring the total radiation emitted, found that with rise in temperature the emissivity of these oxides approached that of a complete radiator. This difference may, of course, be possible, just as in the present examination of the Nernst glower the value of which was found to vary, while Mendenhall and Ingersoll,[1] by using a total radiation method of comparison with platinum, could not establish with certainty any variation of a with temperature. An inspection of figs. 58 and 59 shows that this may be possible, especially in the latter where the energy curve appears to have two maxima. For the "Helion" filament, which is a carbon filament upon which is a deposit of silica, the constant $a=8.3$ when new, and decreases to 6.3 after aging. For tantalum the value of a is 6.5. From the energy curve of the acetylene flame published by Stewart (Phys. Rev. 16, p. 123) the value of a is about 11. A platinum strip, $50 \times 1.5 \times 0.02$ mm. inclosed in a glass bulb with a fluorite window, was also examined. Estimating temperatures from the position

[1] Mendenhall & Ingersoll: Phys. Rev., 25, p. 1, 1907.

of the λ_{max} ($\lambda_{max} T = 2620$) it was found that the "constant" a decreased from $a = 8.5$ at 900° C. to $a = 6.3$ at 1100° C.

Using metal filament lamps (commercial 110-volt) under "normal" working conditions, for metallized carbon $a = 6.1$, for tantalum $a = 6.3$, for tungsten $a = 6.6$, and for osmium $a = 6.9$. In all cases the value of a was found to decrease with rise in temperature.

Theoretically, this variation in a must occur at some stage in the temperature (either an abrupt decrease at some fixed temperature, or a uniform decrease throughout the range), otherwise a temperature would be attainable at which the total radiation is greater than that of a complete radiator at the same temperature.

In the "black body" the reflection is zero. The Nernst glower, as well as the oxides in general, have a very low reflecting power; hence, if the radiating layer is of sufficient thickness, the emissivity of the oxides must be almost as great as that of a "black body," as has just been found for the Nernst glower, at high temperatures. Some oxides, having absorption bands in the visible spectrum, *e. g.*, CeO_2, when in thin layers (Welsbach mantle) and at high temperatures will have a higher luminous efficiency than the same material in thick rods, *e. g.*, the Nernst glower. In the next chapter it will be shown that the greater the electrical conductivity the more continuous will be the emission spectrum of the oxides. Furthermore, mixtures of oxides like mixtures of gases in a vacuum tube have composite emission spectra. This indicates a possible method of analysis of mineral solutions, and it is hoped to make a further examination into this question.

CHAPTER II.

SELECTIVE RADIATION FROM VARIOUS SOLIDS.

INTRODUCTION.

Our knowledge of the emission of radiant energy from various substances with change in temperature is extremely limited, being confined to platinum in the case of metallic electrical conductors, to several gases in vacuum tubes, to water-vapor and carbon dioxide in the Bunsen flame, to carbon, to the oxides of copper and iron, and to the radiation from a uniformly heated cavity or complete radiator. The emission spectra of the Bunsen flame and of gases in vacuum tubes were found to be composed of sharp emission bands superposed upon a weak continuous spectrum. The solids were found to have smooth continuous emission spectra, and it seems to be the general expectation to find (see Kayser's Spectroscopie, vol. 2, pp. 135 and 284, also Rudorf, Jahrb. Radioakt. und Elektronik, 4, 385, 1908) that all solids emit continuous spectra.

To Paschen is due the credit for the first systematic study of the spectral distribution of radiant energy from various solids, and from the Bunsen flame. Subsequent work by others has been but little more than the establishment of the so-called radiation constants to a greater number of significant figures than was possible by Paschen, with the facilities at his disposal. Great credit is due to Lummer and Pringsheim for establishing the limits within which the radiation laws, notably Wien's law, hold. It must be said, however, that Paschen had these limits partly established; but he insisted that the discrepancies between theory and experiment were due to errors of observation. In this brief summary it is not possible to present the subject fully, but after working over the data, one can not help feeling that it is extremely unfortunate that the results of these investigations are beclouded with controversies as to whom belonged the credit for doing or suggesting this, that, or some other thing in connection with the work.

The best proof of Kirchhoff's law of the proportionality of emission and absorption is due to Paschen,[1] who found that the intensity of the emission of the CO_2 band at 4.4 μ, when using a column of gas 7 cm. long, was as great as for a column of gas 33 cm. long. In other words, the intensity of the radiation was as great as that of a complete radiator for the same

[1] Paschen: Ann. der Phys. (3), **53**, p. 26, 1894.

wave-length and at the same temperature. Unfortunately the number of radiating substances of which it is possible to determine even an approximate temperature is extremely small. Hence, the work presented on the following pages can not be more than a qualitative proof of Kirchhoff's law of proportionality between emission and absorption. It has numerous applications, however, particularly in studying substances having sharp emission (hence sharp absorption) bands. Numerous substances are given here, of which it has not been practicable to study the absorption spectra. Their emission spectra give us some idea of the nature of their absorption, the only difference being that the emission bands are more intense, due to the greater thickness (and the higher temperature) of the substance examined. Another feature of the results obtained, which is new, is the extreme sharpness of the emission bands. Moreover, the maxima of the emission and absorption bands coincide, although the temperatures at which the two sets of observations were made differ by 800 to 1000° C. The positions of the sharp, well-defined maxima are not affected by change in temperature. This is in marked contrast with the results of Königsberger[1] for the limited region of the visible spectrum, in which he found that for certain selectively absorbing substances the maximum of the absorption band shifts toward the long wave-lengths with rise in temperature, and with the results of Paschen on the emission bands of CO_2 and water-vapor, which shifted with rise in temperature, some toward the long, others toward the short wave-lengths. The data may also prove to be of use in determining whether pleochroism is an inter- or intra-molecular phenomenon. For example, the absorption spectrum of adularia shows a band at 3.2 μ, which in the emission spectrum is shifted to 2.9 μ. The latter band is characteristic of silicates, whether in the emission or absorption spectrum. The present work may be considered an examination of the emission spectra of electrical insulators, or transparent media. The only previous work done on this subject is due to Rubens,[2] who examined the radiation from the Auer mantle, as well as mantles composed of the pure oxides of cerium and of thorium. The difficulty experienced by him was the elimination of the emission spectrum of the hot gases which was superposed upon that of the oxides composing the mantle. Hence, if he had examined a mantle of zirconium oxide he would not have been able to detect an emission band which occurs at 4.3 μ.

The substances used in the present investigation were in the form of solid rods made in an oxy-hydrogen flame or in the form of thick layers of the substance placed upon a heater. The rods were heated by an electric current from the secondary of a 2000-volt (300-watt) transformer. These rods had, of course, to be heated initially with an alcohol or blast lamp until they became conducting, just as is necessary with the Nernst glower.

[1] Königsberger: Ann. der Phys. (4), 4, p. 796, 1901.
[2] Rubens: Phys. Zs., 6, p. 790, 1905.

The resistance placed in the primary circuit of the transformer to regulate the current, and the low capacity of the transformer, acted as a "ballast" to the radiating substances. The rods were provided with platinum terminals, sealed in the ends, and were securely mounted in incandescent lamp sockets. After heating them until they became conducting, they were mounted securely before the spectrometer slit. The substances that could not be melted and formed into rods were made into a paste and spread upon the "heater tube" of a Nernst lamp. The "heater tube" consisted of a hollow porcelain tube about 5 cm. long and 8 mm. diameter covered with a coil of fine platinum wire, and was used in preference to a platinum strip on account of its rigidity and ease in handling. It gave the same results as the same material on a platinum strip. The spectrometer, the fluorite prism, and the bolometer were previously used in examining the Nernst glower. It is important to notice, however, that by inclosing the optical parts of the instrument it was possible to entirely eliminate the atmospheric absorption bands, which had not been done successfully by previous experimenters. The emission curves are, therefore, within experimental errors, an exact portrayal of the distribution of the energy emitted in different parts of the spectrum. Unfortunately it is not possible to determine the temperature of the radiating body, the thickness of which would have to be specified, in many cases. A thermocouple can not be applied on account of the loss of heat by conduction. It is, of course, absurd to attempt to measure temperatures with an optical pyrometer. For example, the rod of oligoclase was a perfectly transparent glass, and emitted no light other than that due to sparking of the platinum terminals, although at a temperature of 1100 to 1200° C. Nevertheless, a substance such as iron oxide would have emitted light when at the same temperature, while both emit strongly in the infra-red. A further example is the rod of topaz, which was an opaque white mass. On withdrawing it from the oxy-hydrogen flame, it was accidentally stroked with the iron forceps, when the parts so stroked emitted a dull red light, due to the greater emissivity of the iron oxide, while the untouched parts retained their usual white color.

Instead of temperatures, the energy consumption is given; also the dimensions of the rods, the lengths being the distances between the platinum terminals. The diameters are in some cases not very accurate, owing to the irregularity of some of the filaments. The voltage was measured with an electrostatic voltmeter, joined to the terminals of the rod. The current was measured with a milliammeter, of a suitable range to insure accuracy.

It is manifestly impossible to have the smoothness of the surface and the thickness of the radiating layer the same for all substances. The distance (about 2 cm.) of the radiator from the slit and the bolometer sensibility will also vary. No attempt has therefore been made to obtain the emission curves of the various substances at the same temperature,

and to plot them to the same scale. The purpose of the present examination is to map the distribution of energy in the various spectra, hoping that at some future time it may be possible to make a more extended study of certain substances which show unusual emission spectra.

RADIATION FROM ELECTRICALLY HEATED SOLIDS.

Prominent among this group are a series of silicates, which have an emission band in common at 2.88 μ (characteristic of SiO_2) which is as

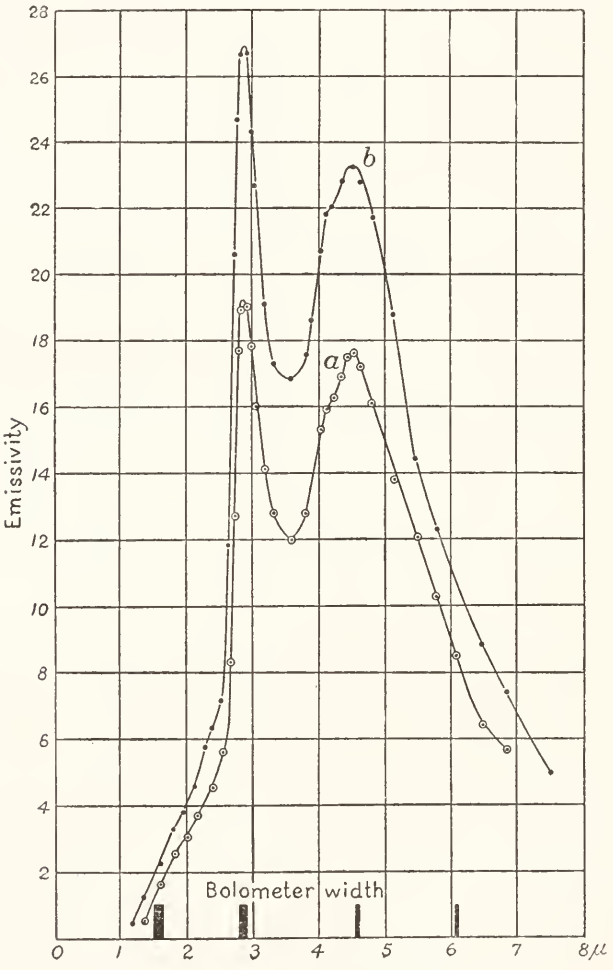

FIG. 63. — Emission spectrum of albite.

sharp as any yet found in gases. The absorption spectra of many of these compounds are recorded in Part III of these investigations (Carnegie Publication No. 65).

In order to give the reader some idea of the conditions under which

the data was obtained, a rough estimate is made of the temperature at which a complete radiator would emit light of a color similar to that given out by the substance under investigation. The fact that soot from the gas flame was burned off the rods not emitting light would indicate that the temperature was above 600° C., and in all cases the estimated temperature is greater than 800° C.

The length of the rods used depended upon the melting-point. For example, the "soft glass" rod was very short on account of its softening at the temperature necessary to keep it electrically conducting. The ends of the rods were shielded from the spectrometer slit. All these curves are reduced to the normal spectrum by dividing the observed galvanometer deflections by the slit-width expressed in wave-lengths. In this work the unsteadiness of the bolometer prevented an accurate mapping of small emission bands occurring beyond 6 μ.

ALBITE ($NaAlSi_3O_8$).

(Rod 8 mm. long, tapering from 1.8 to 2.8 mm. in diameter. Energy supplied, 7.1 and 8.2 watts. Curves *a* and *b*, fig. 63. Temperature 800°. Transmission given in Carnegie Publication No. 65, p. 65.)

The rod was translucent and seemed to emit no light except that reflected from the platinum terminals. The emission band at 2.88 μ is

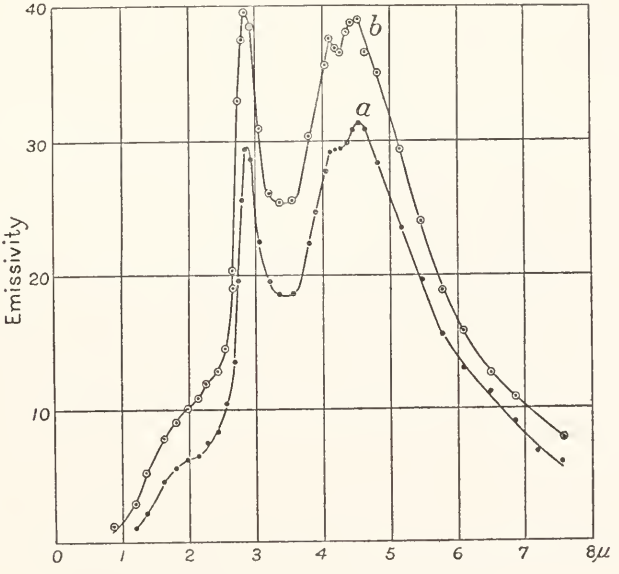

FIG. 64. — Emission spectrum of orthoclase (var. adularia).

more intense than the one found in orthoclase, just as was found in the absorption spectrum. Two other bands are noticeable at 4.1 and 4.5 μ, respectively.

ORTHOCLASE (var. ADULARIA) [$KAlSi_3O_8$].

(Rod 8 mm. long, 2 mm. diameter. Energy supplied, 6.2 and 8.9 watts. Curves *a* and *b*, respectively, of fig. 64. Transmission, Carnegie Publication No. 65, p. 64.)

This substance emitted a little more light than albite, although it was more transparent. The emission band at 2 μ is prominent. The one at

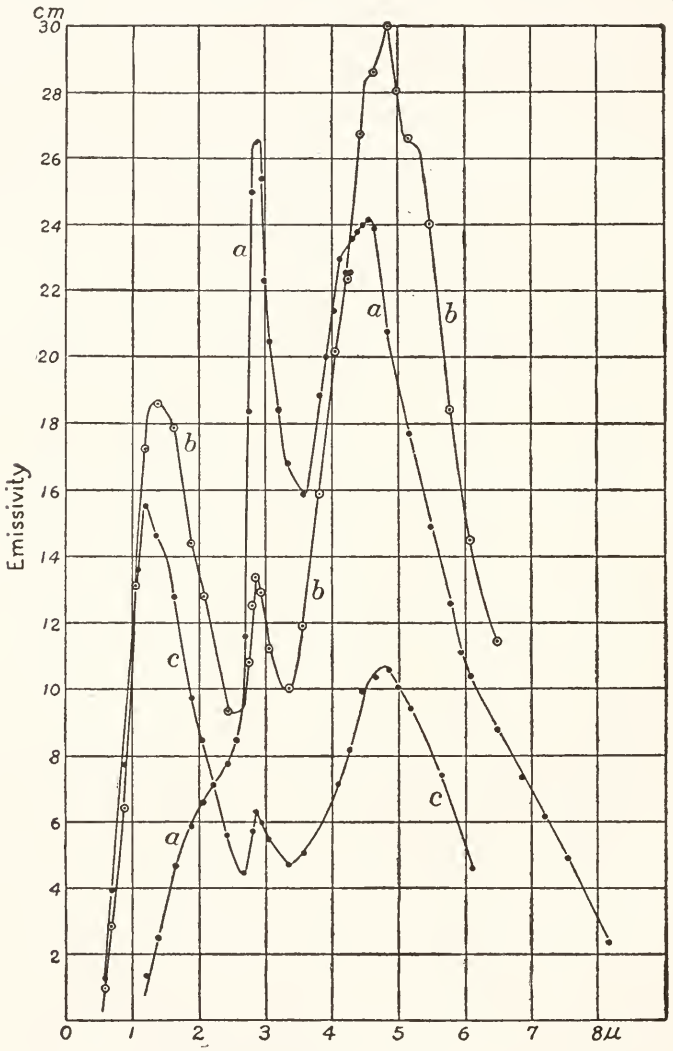

FIG. 65. — Orthoclase (*a*); alumina and silica (*b*); alumina and feldspar.

2.88 μ is shifted from its position at 3.2 μ in the absorption spectrum, from which it would appear that the group of atoms causing the absorption is different in the two cases. An examination of the transmission spectrum using polarized light will be necessary to determine the true

position of the absorption band. The band at 4.1 and 4.5 μ are in common with the other feldspars.

ORTHOCLASE (FELDSPAR) [$KAlSi_3O_8$].

(Rod 7 by 2.2 mm. Energy, 7.5 watts. Curve *a*, fig. 65. Transmission, Carnegie Publication No. 65, p. 64.)

This sample was translucent, due probably to air-bubbles. Its color on 7.5 watts was slightly red, due in part to reflected light from the elec-

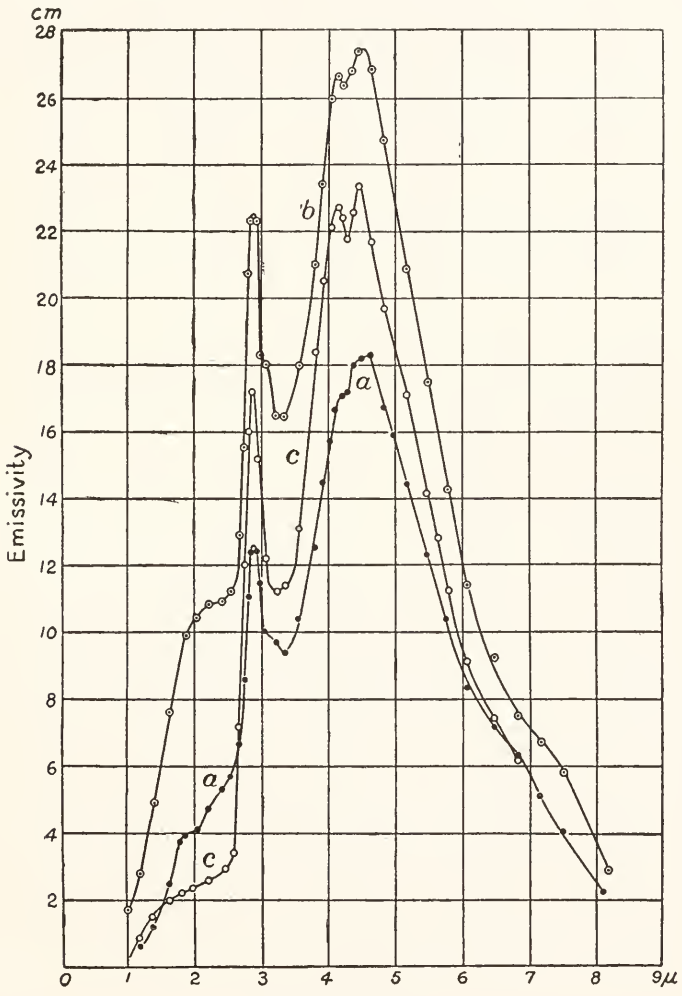

FIG. 66. — Oligoclase.

trodes. The emission bands at 2, 2.88, 4.1, and 4.5 μ are in common with the preceding, with the possibility of a small band at 3.1 μ, to be noticed in fig. 66.

OLIGOCLASE $\left\{ \begin{matrix} 3\,NaAlSi_3O_8 \\ CaAl_2Si_3O_8 \end{matrix} \right\}$

(Rod 9 by 2.8 mm. Energy supplied. Curve $a = 8.6$, $b = 13.3$, and $c = 29.4$ watts. Curves *a* and *b*, fig. 66. Transmission, Carnegie Publication No. 65, p. 64.)

The original crystal, as well as the glass rod, were perfectly transparent. The rod showed no color on suddenly throwing off the current. The platinum terminals melted on 16 watts, *but the rod showed no color.* As in the preceding feldspars there are bands at 2, 2.88, 3.1, 4.1, 4.5, and 7 μ. The absorption band at 4.8 μ seems to be shifted to 4.5 μ in the emission spectrum. Curve *c* shows the distribution of energy when the rod (another sample, plotted to a different scale) was heated until viscous, see fig. 91.

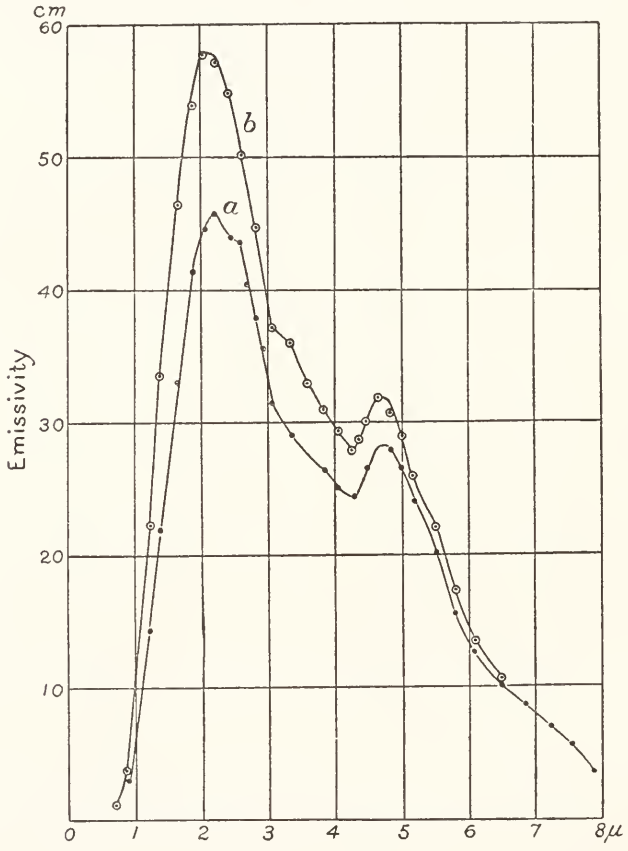

FIG. 67. — Amphibole.

AMPHIBOLE (TREMOLITE?) [$CaMg_3(SiO_3)_4$].

(Rod 6 by 1.5 mm. Energy supplied, 2 (?) and 4.8 watts. Curves *a* and *b*, fig. 67. Transmission, Carnegie Publication No. 65, p. 64.)

At the highest energy consumption the color of the filament was a light yellow, corresponding to a temperature of 1200 to 1300°. The emission

curve is quite different from the preceding, due in part to the higher temperature. The absorption band at 6 μ appears as a depression in the emission spectrum.

WOLLASTONITE ($CaSiO_3$).

(Rod 10 mm. long, tapering from 3 to 4 mm. diameter. Energy supplied, 18 watts. Curves *a* and *b*, fig. 68.)

This rod was made from a pure transparent glass, supplied by Dr. Allen of the Geophysical Laboratory of the Carnegie Institution of Washington, which became a white crystalline mass on melting in the oxy-hydrogen flame. It was rendered conducting with difficulty, and could not be heated uniformly.

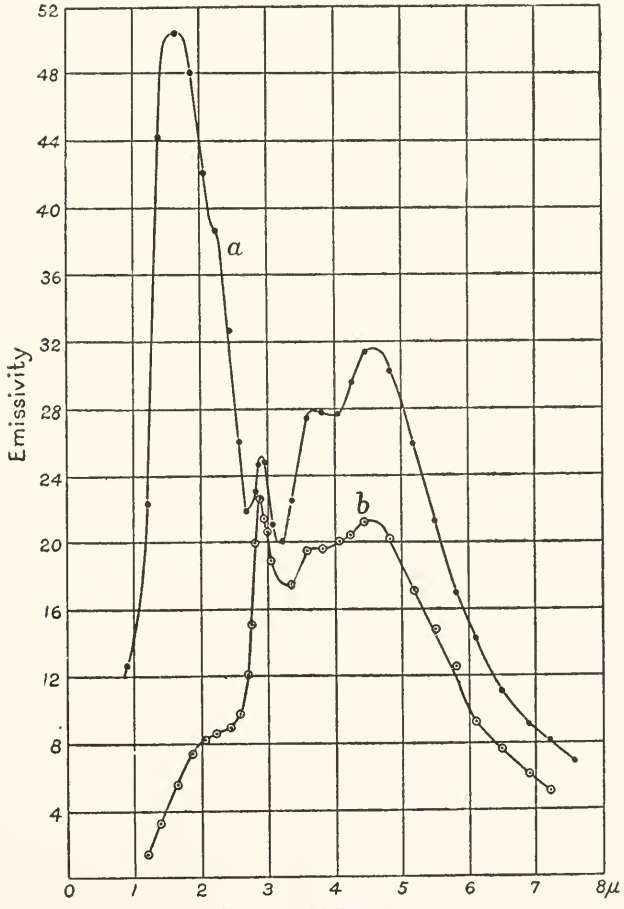

FIG. 68. — Wollastonite.

The silicate band at 2.9 μ is prominent, while a new band appears at 3.7 μ. Curve *b* gives the emission from the coolest side of the rod, while curve *a* represents the emission from the hottest side. The latter is an excellent illustration of the rapid increase in intensity with temperature,

of the emission bands on the side of the spectrum toward the short wave-lengths. Further examples will be found in figs. 77 and 78. In this and in the preceding substance the emission bands are not so sharp as usual, which may be due to the greater molecular weight of the base.

PORCELAIN (PYROMETER TUBING).

(Hollow rod 15 by 2 mm. (hole 1 mm.). Energy supplied, 9.2 watts. Fig. 69.)

The sample of pyrometer tubing examined was heated to a light-red color (1400°) to keep it conducting. The energy spectrum is marked for

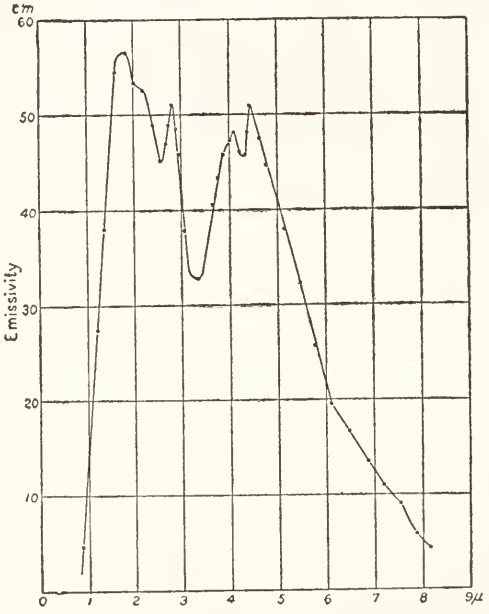

FIG. 69. — Porcelain.

its strong emission, with sharp maxima at 1.8, 2.1, 2.83, 3.7, 4.1, and 4.5 μ, and with indications of bands beyond 6 μ. Porcelain is made from a hydrous aluminum silicate.

GLASS ("SOFT GLASS").

(Rod 3 by 2 mm., heated to dull red color. Curve *a*, fig. 70. Transmission, Carnegie Publication No. 65, p. 65.)

The substance examined was a piece of ordinary "soft" white glass tubing, drawn into a solid rod. There are emission bands at 2, 2.86, 3.6, 4.4, and 5.5 μ.

MAGNESIA (PYROMETER TUBING).

(Hollow rod, 12 by 1.5 mm. (hole 1 mm.). Energy supplied, 6.6 watts. Curve *b*, fig. 70.)

This material is used to insulate thermo-couples, and conducts only at high temperatures. It is probably a mixture of magnesium oxide (see fig. 80) and silica. The temperature was probably 1200° to 1400°. The

emission spectrum is conspicuous for two regions of strong emissivity at 1.6 and 5 μ, respectively, with a deep depression at 3.5 μ. The emission bands at 1.6, 2.7, 5, 5.5, and 7.1 μ are not well resolved, but their presence can not be doubted.

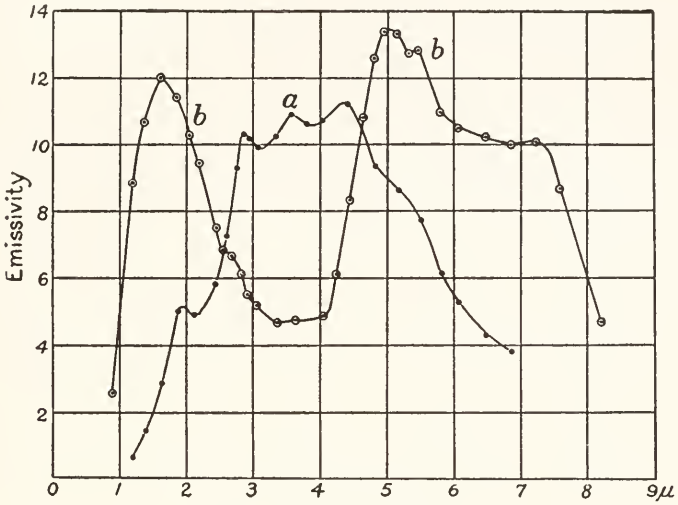

FIG. 70. — Glass (*a*); Magnesia.

GLASS (COBALT BLUE).

(Rod 12 by 2 mm. Energy supplied, 5.4 and 7.5 watts. Curves *a* and *b*, fig. 71.)

This rod was heated to a dull red. The emission spectrum is quite different from that of soft glass, but there are not such prominent bands

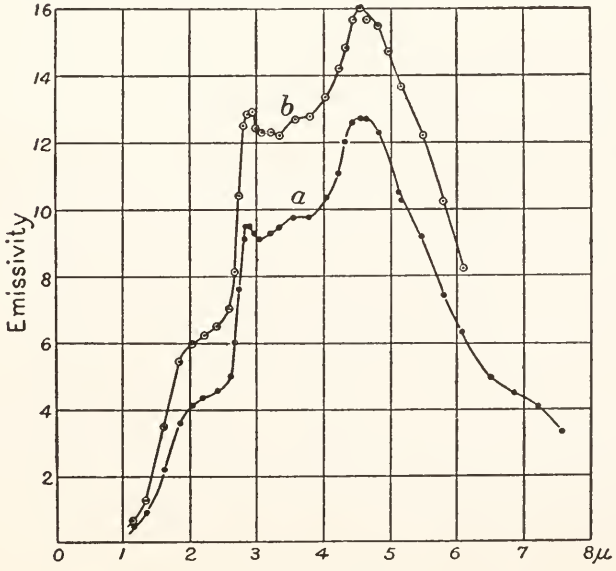

FIG. 71. — Cobalt glass.

MARINE BIOLOGICAL LAB. WOODS HOLE LIBRARY MASS.

as one might expect from a knowledge of the absorption bands at 1.6 and 2.2 μ to be noticed in fig. 37. The silicate band at 2.87 μ is prominent. Other bands occur at 2, 3.6, 4.6, and 5.5 μ, respectively.

SPODUMENE [$LiAl(SiO_3)_2$].

(From Pennington County, South Dakota. Irregular rod, 12 by 1.5 mm. Energy supplied, 5.7 and 9.5 watts. Curves *a* and *b*, fig. 72.)

This mineral contains cerium, lanthanum, and other "rare earths" as impurities. It can be melted in a blast flame. Considerable light was emitted, due to the presence of impurities. The emission spectrum shows the silicate band, sharply defined at 2.88 μ, with other bands at 2, 4.1, 4.5, 4.9, and 6.5 μ.

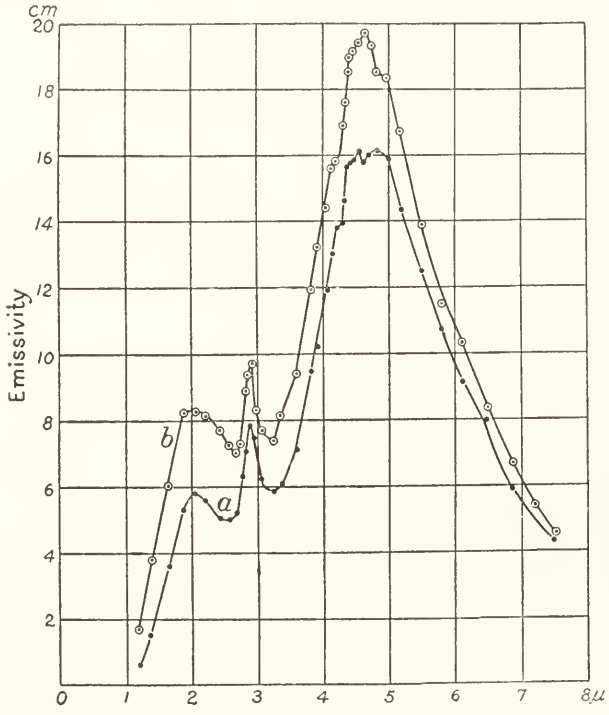

FIG. 72. — Spodumene.

BERYL [$Be_3Al_2(SiO_3)_6$].

(Rod 10 by 3 mm. Energy, 7 to 8 watts. Curve *a*, fig. 73.)

The rod was an opalescent milky glass, although the original crystal was a transparent green. The temperature was probably 1100°. The emission spectrum is unusual in appearance, with a sharp maximum superposed upon it at 2.8 μ. Other ill-defined maxima appear to be at 1.7, 2.4, 2.9, 3.6, 4.4, and 4.8 μ.

RUTILE (TiO_2).

(Flat plate 8 mm. long, tapering from 1.5 to 1.8 mm. wide and 0.25 mm. thick. Energy supplied, 6 watts. Curve *b*, fig. 73. Transmission, Carnegie Publication No. 65, p. 67.)

This mineral was heated to a bright red color corresponding to a temperature of perhaps 1000°. The emission spectrum shows maxima at 2.4, 3.2, 5,5, and 7.0 μ. The transmission spectrum is too low to show these as absorption bands; but the band at 3.1 μ is visible in the transmission spectrum of brookite (TiO_2). This substance is a good conductor of electricity at this temperature, but a very poor radiator of light rays.

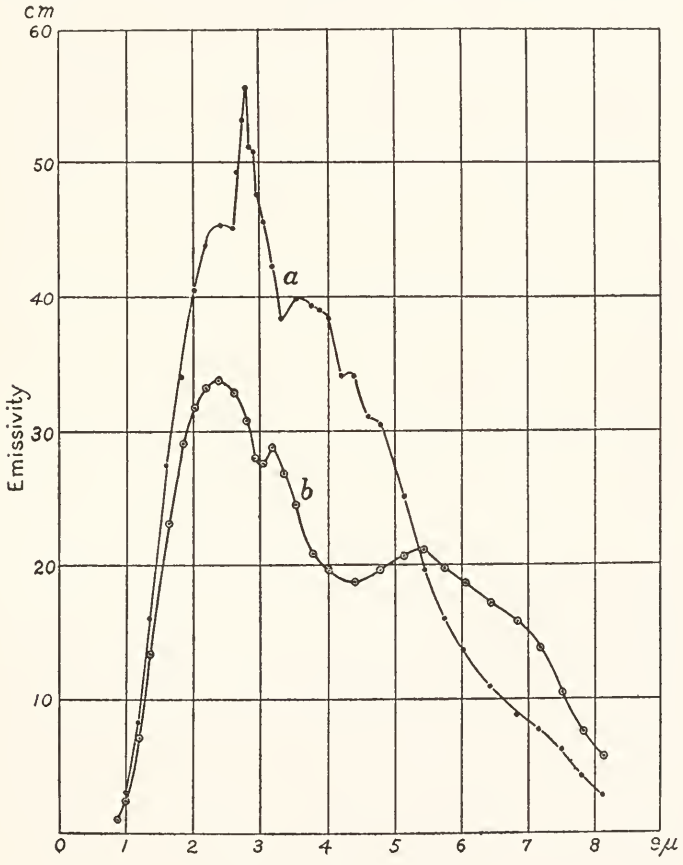

FIG. 73. — Beryl (*a*); Rutile.

TOPAZ [$(AlF)_2SiO_4$].

(Rod 13 mm. long, 2 to 2.5 mm. diameter. Energy supplied, 0.05 and 0.07 ampere, — probably 15 to 21 watts. Curves *a* and *b*, fig. 74.)

This rod was built up from the massive transparent mineral, and rendered conducting by the vapor set free from the albite cement used to secure the platinum terminals to the rod. The vapor left a narrow con-

ducting streak along one side of the rod, which heated the topaz. The curve is conspicuous for the sharpness of its emission bands, which occur at 1.4, 2.85, 4.1, 4.5, and 7.5 μ.

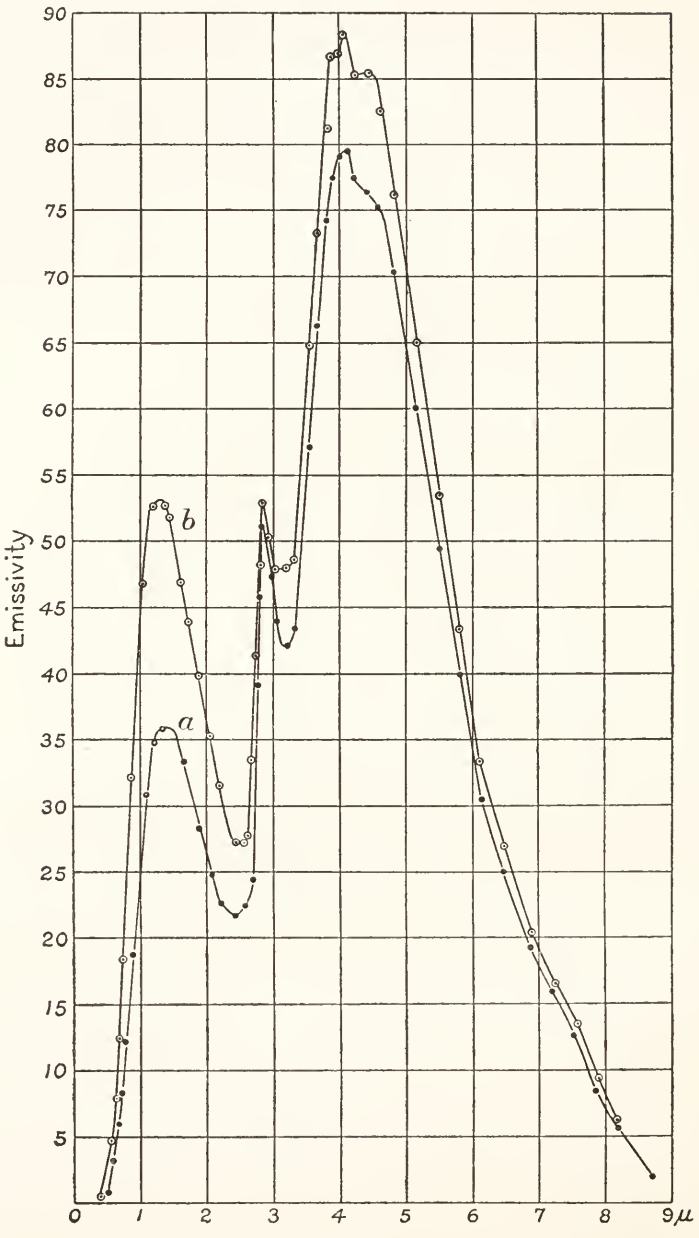

FIG. 74. — Topaz.

APATITE [$Ca_5F(PO_4)_3$].

(Rod 12 by 1.5 mm. Energy supplied, 9.3 and 11.8 watts. Curves *a* and *b*, fig. 75. Transmission, Carnegie Publication No. 65, p. 58.)

The emission spectrum shows emission bands at 2.9 and 4.5 μ. The rod was made from a dark massive specimen which may have contained silica, whence the band at 2.9 μ in both the emission and absorption spec-

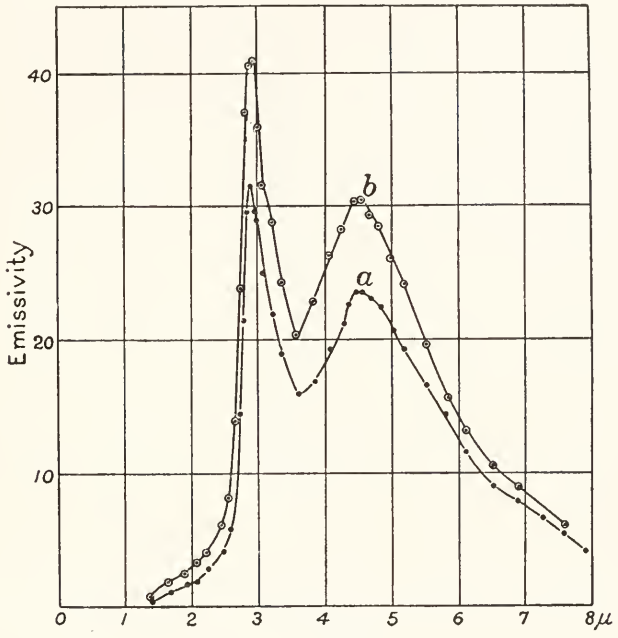

FIG. 75. — Apatite.

trum. On the other hand, many oxides, known to be free from silica, have a strong emission band in this region, from which it would appear that this band is characteristic of the oxides.

ALUMINUM OXIDE (Al_2O_3).

(Rod 14 mm. long, tapering from 2.5 to 3 mm. in diameter. Energy supplied, 0.025 and 0.115 ampere. Curves *a* and *b*, fig. 76.)

The rod was built up from the pure powder in an oxy-hydrogen flame. The emission curve is conspicuous for the great variation in intensity of its emission bands which occur at 1.4, 2, 3.1, 4.7, 5.2, and 7.5(?) μ. The emission curve differs but little from the one of topaz except that the latter has the silicate band at 2.85 μ. In fig. 65, curve *c* shows the radiation from a rod made from alumina and 1 per cent of feldspar, and curve *b*, fig. 65, gives the radiation from a rod made of alumina and 1 per cent of silica. In both cases the silica band at 2.87 μ is superposed upon the spectrum of the aluminum oxide.

ZIRCONIUM OXIDE (ZrO_2).

(Rod 5 by 1.4 mm. Energy consumption, 3.5 (900°), 4.8, 5.8, 7.5 watts, curves *a*, *b*, *c*, *d*, fig. 77; 9.6, 12.1, and 14.5 (1400°) watts, curves *a*, *b*, *c*, fig. 78.)

The specimen examined was a fragment from a furnace wall. It probably contained some "binder," although from the curve for the pure

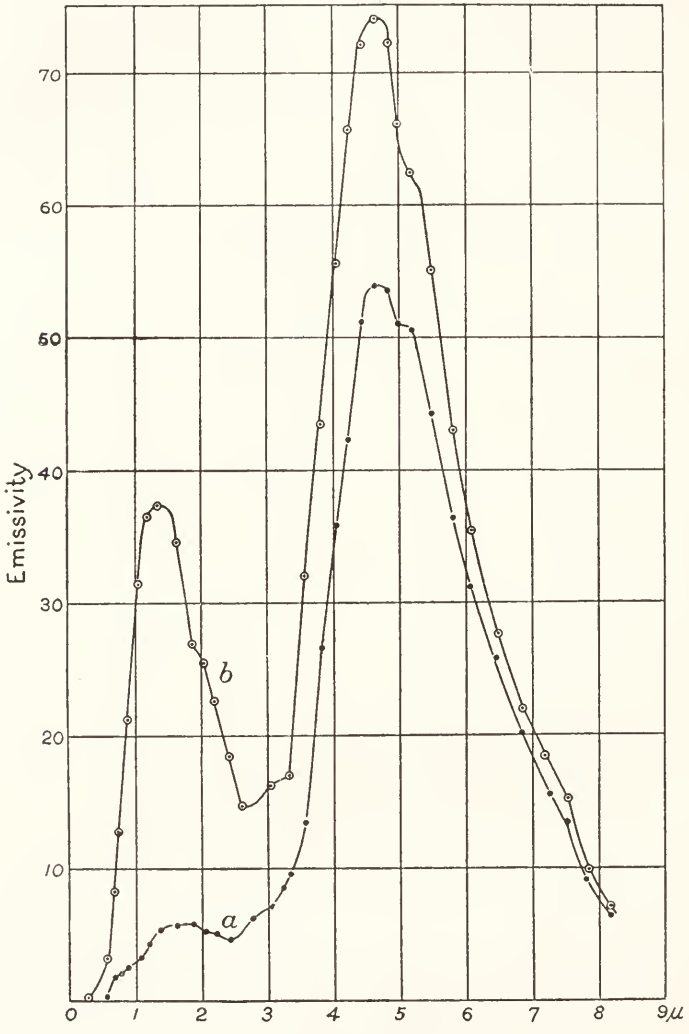

FIG. 76. — Aluminum oxide.

material (fig. 79) the foreign substance contributed but little to the emission bands. The fine platinum terminals were wound around the ends of the rod which was about 10 mm. long (5 mm. between the terminals).

The curves are conspicuous for their sharp emission band at 4.3 μ,

which remains superposed upon the continuous background even at a bright yellow heat, corresponding to a temperature of about 1400°.

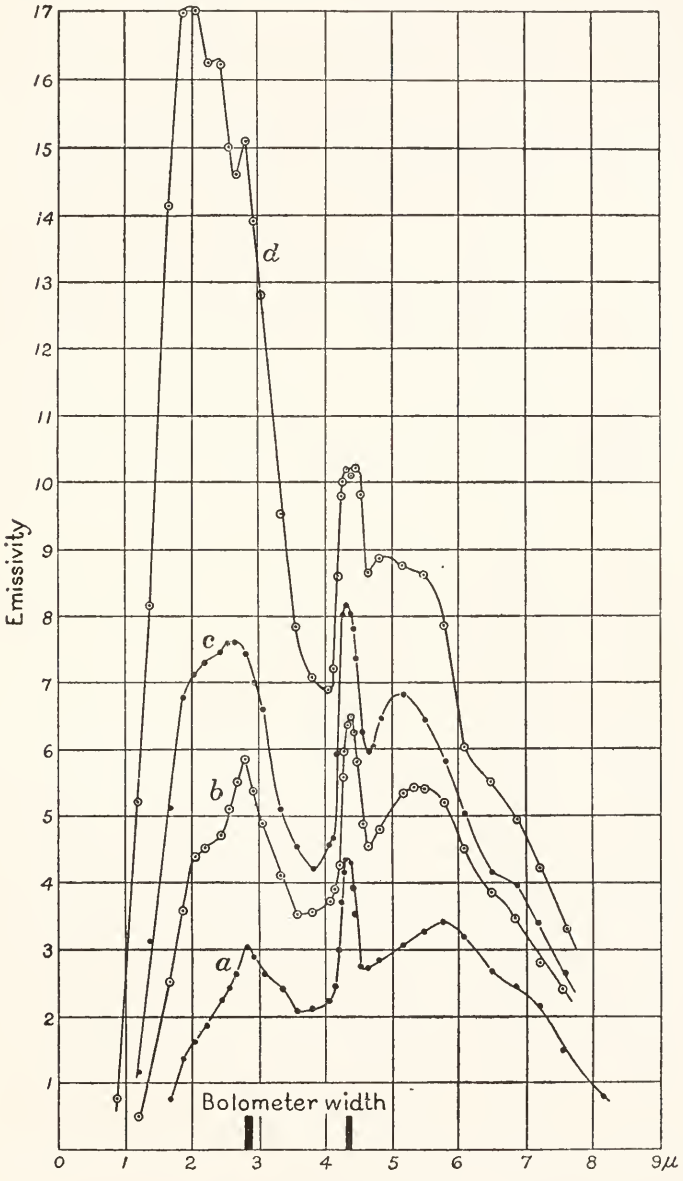

FIG. 77. — Zirconium oxide.

This series of energy curves is one of the best illustrations yet recorded of the gradual shift of the maximum of intensity of emission toward the short wave-lengths with rise in temperature. On an energy consumption

of 3.5 watts, the maximum of the envelope of these emission bands lies at 4 to 5 μ, and shifts steadily to the short wave-lengths, being at about 1.8 μ for an energy consumption of 14.5 watts. The pure oxide is not an efficient radiator of white light, and only becomes so when a small amount of cerium or thorium oxide is added, which combination is the Nernst glower already

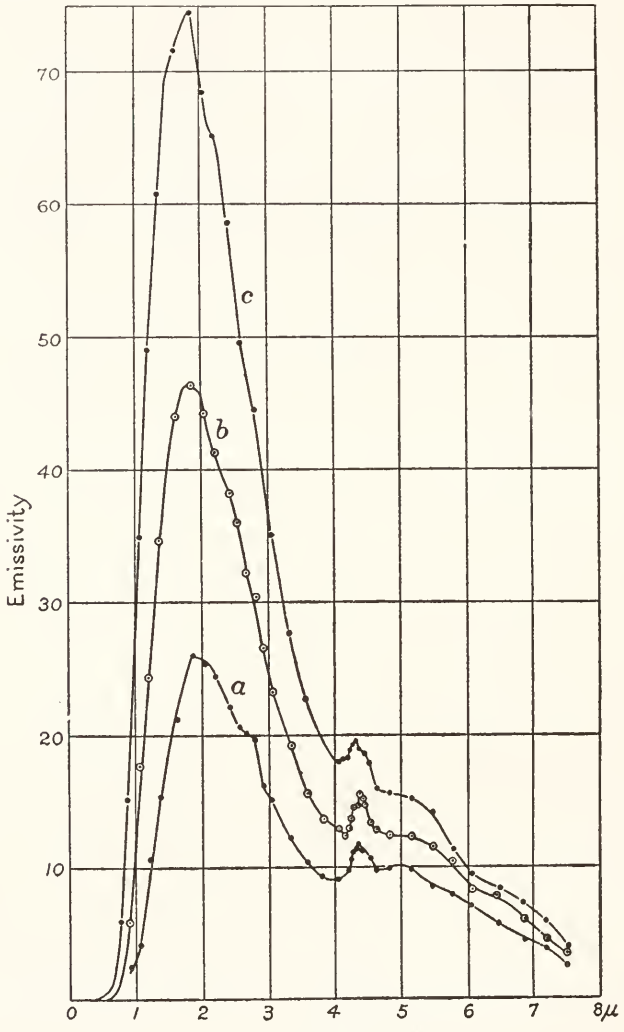

FIG. 78. — Zirconium oxide.

mentioned. Aside from the sharp emission lines at 2.8 and 4.35 μ there are wide hazy bands at 2 and 2.4 μ (appears on 7.5 watts), while from 5 to 6 μ there is a wide band which is evidently unresolved, the maximum shifting toward the short wave-lengths with rise in temperature. The extraordinary rapidity which characterizes the growth of the emissivity at

1.5 to 2 μ is worthy of notice. In one case where the ratio of emissivity at 4.3 μ for a given increase in energy is 50, it is almost 200 at 2 μ. In fig. 77 the curves are all for practically the same sensibility, 71, of the instrument. In fig. 78 the sensibility of the instrument was 60. These units are arbitrary, being the galvanometer deflections obtained by unbalancing the bolometer by a constant amount. For this substance the radiating rod was short and the voltage too low to be measured with the electro-static voltmeter. The ordinary voltmeter used affected the temperature of the radiator slightly, so that the energy consumption recorded is not so accurate as in the other observations.

EMISSION SPECTRA OF SOLIDS ON NERNST "HEATER TUBE."

In examining the radiation from solids placed upon a heater it is possible to have some of the radiation from the latter transmitted through the former. If the substance to be examined is in the form of a fine powder and the layer is from 0.5 to 1.5 mm. thick there is but little chance for the radiation to be transmitted from the heater. This fact enables one to study the selective emission of solids which can not be formed into solid rods, and is applied in studying the following list of substance.

Zirconium Oxide (ZrO_2).

(Layer of oxide 0.8 to 1.5 mm. thick, on Nernst heater tube from which the clay covering had been removed. Fig. 79, curves *a*, *b*, and *c*.)

The zirconium oxide was heated to a dull red, which was somewhat lower than for the rod heated electrically (curve *a*, fig. 77). Curves *a* and *c* give the emission of different samples of the commercial product, the electrical properties of the latter being very bad when used for the body of a glower. Curve *b* shows the emission of a sample which has good electrical properties. It contained less than 0.01 per cent of silica, and was the purest obtainable sample. From this it is evident that the sharp maxima are not due to silica. The emission spectra are very similar and are conspicuous for two sharp emission bands, with maxima at 2.78 μ (curve *a*, maximum at 2.83 μ) and at 4.3 μ, respectively. Smaller maxima appear at 2, 2.4, 3.2, 4.7, and 5.4 μ. From a comparison of these curves with those given in figs. 77 and 78 it appears that in the latter sample the "binder" used, probably yttria, has but little influence upon the sharp emission bands.

Magnesium Oxide (MgO).

(Curve *c*, fig. 80.)

The magnesium oxide (curve *c*, fig. 80) spectrum shows two wide bands at 3 and 5.3 μ, respectively, with a smaller band at 2.1 μ. Somewhat similar conditions were observed in fig. 70.

In fig. 80, curve *a* gives the emission spectrum of the material used in a Nernst glower placed upon a heater-tube. The general outline, and

especially the emission bands, are to be observed in the radiation curves of the glower, given in fig. 57. In curve *b*, fig. 80, is shown the emission spectrum of a commercial "heater-tube." The covering is some refractory substance, perhaps containing aluminum oxide and a silicate binder. There is a sharp band at 2.85 μ and hazy bands at 4.7, 5.3, and 6.3 μ.

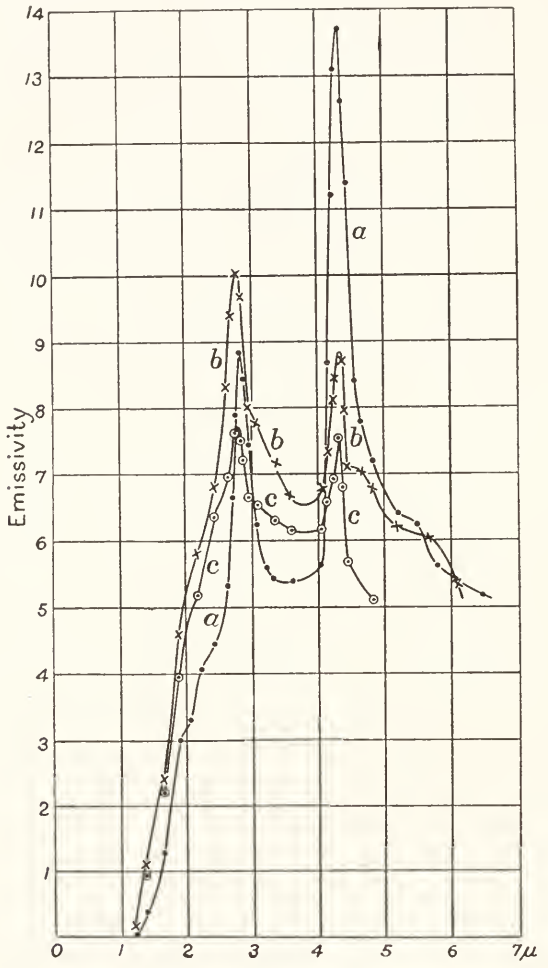

FIG. 79. — Zirconium oxide.

URANIUM OXIDE (U_2O_3); CERIUM OXIDE (CeO_2); THORIUM OXIDE (ThO_2).
(Curve $a = U_2O_3$; $b = ThO_2$; $c = CeO_2$; fig. 81.)

The uranium oxide is a greenish-brown powder which gives a smooth continuous spectrum with hazy maxima at 2.8 and 3.4 μ, respectively.

The thorium oxide, curve *b*, shows no marked emission bands, and the whole spectrum is suppressed to 7 μ. Beyond this point the emissivity is

high, corresponding closely to that of a complete radiator, as was shown by Rubens, using a gas-mantle of this material.

The cerium-oxide curve shows a strong emission at 2 to 3 μ, as was found by Rubens, with possible bands at 4.4 and 7.5 μ. It was shown by Rubens that beyond 7 μ the emissivity approaches that of a complete radiator.

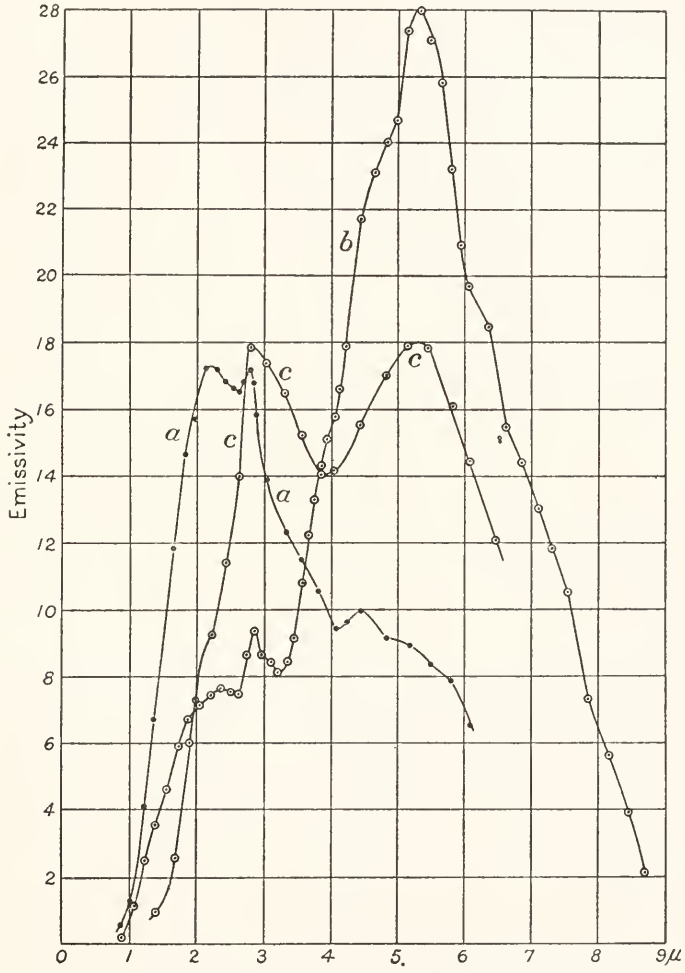

FIG. 80. — Nernst glower (*a*); Nernst "heater-tube" (*b*); Magnesium oxide.

In the Auer gas mantle (90 per cent ThO_2 + 1 per cent CeO_2) the cerium oxide acts as a sensitizer does on a photographic plate, by making an absorption band in one region of the spectrum without affecting the rest.

The energy curve of an electrically heated filament of the same composition as the Auer mantle is given in the Bulletin of the Bureau of Standards, vol. 5, No. 2, 1908. The energy curve is entirely different

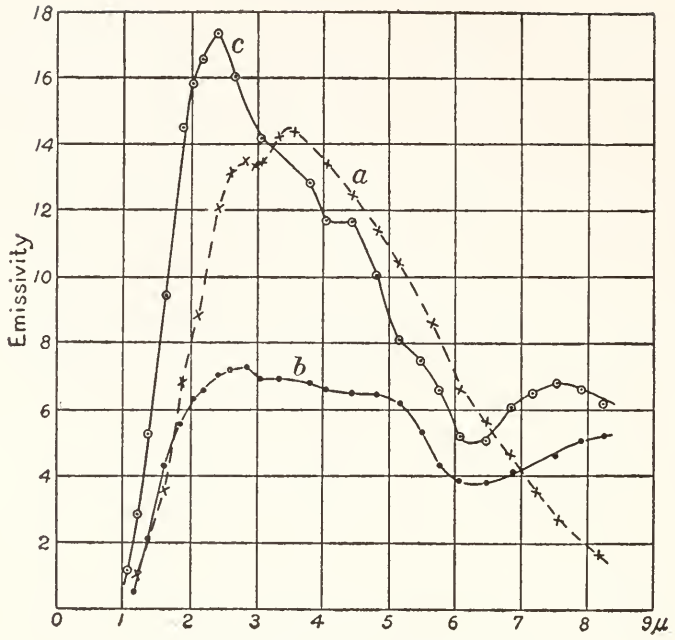

FIG. 81. — Uranium oxide (*a*); Thorium oxide (*b*); Cerium oxide.

from that of the Auer mantle, being similar to that of the Nernst glower. This is no doubt due to the greater thickness of the radiating layer, which emits a more nearly saturated radiation in the region of 1 to 3 μ, as well as in the remainder of the spectrum.

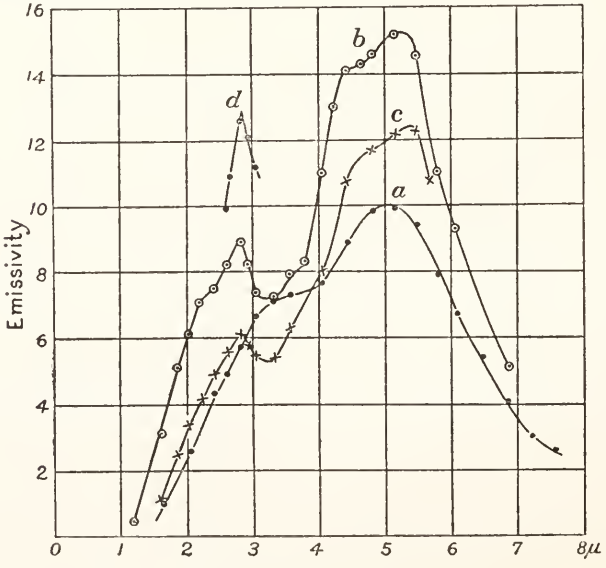

FIG. 82. — Beryllium oxide (*a*); Silica (*b*), (*c*); Feldspar.

BERYLLIUM OXIDE (BeO); SILICON OXIDE (SiO_2); VANADIUM OXIDE (V_2O_6).

(Curve a=BeO; b and c=SiO_2; fig. 82.)

The beryllium-oxide emission spectrum is smooth, with two wide maxima at 3.5 and 5 μ, respectively. The temperature was such that a faint red showed through the interstices of the layer of white oxide.

The silicon-dioxide (quartz, French flint) curve shows bands at 2.2, 2.83, 3.7, 4.4, and 5.3 μ, which coincide with the absorption bands (see Carnegie Publication No. 65, p. 21). For curve c the layer of silica was 1.4 mm. For curve b (thinner layer) the surface temperature was about 800°.

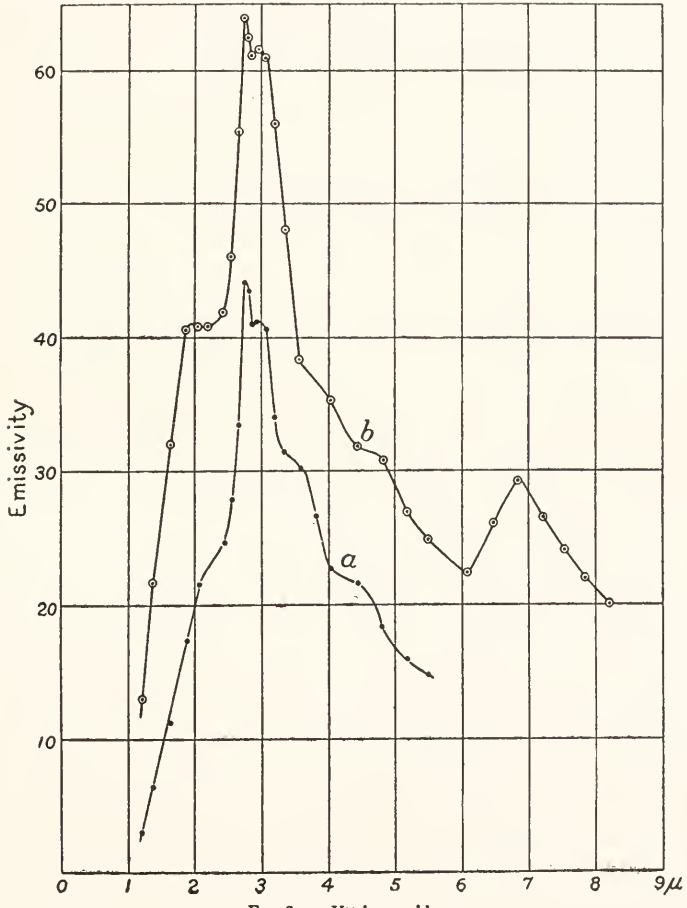

FIG. 83.—Yttrium oxide.

The vanadium oxide in the preliminary examination showed no emission bands. The substance is a black powder, which melted at a low red heat, and no further examination was made into its emission spectrum, which was similar to that of carbon. Curve d, fig. 82, shows the emission band of pure feldspar placed on the heater.

YTTRIUM OXIDE (Y_2O_3).

(Curves *a* and *b*, fig. 83; curves *a*, *b*, *c*, fig. 84.)

The surface color in the two cases (fig. 83) was a deep and a bright red, corresponding to a temperature of 900° to 1000°. The two curves are similar in appearance, showing emission maxima at 2, 2.76, 3, 3.6, 4.6, and 6.9 μ, respectively, the latter band being unusually sharp. It will be

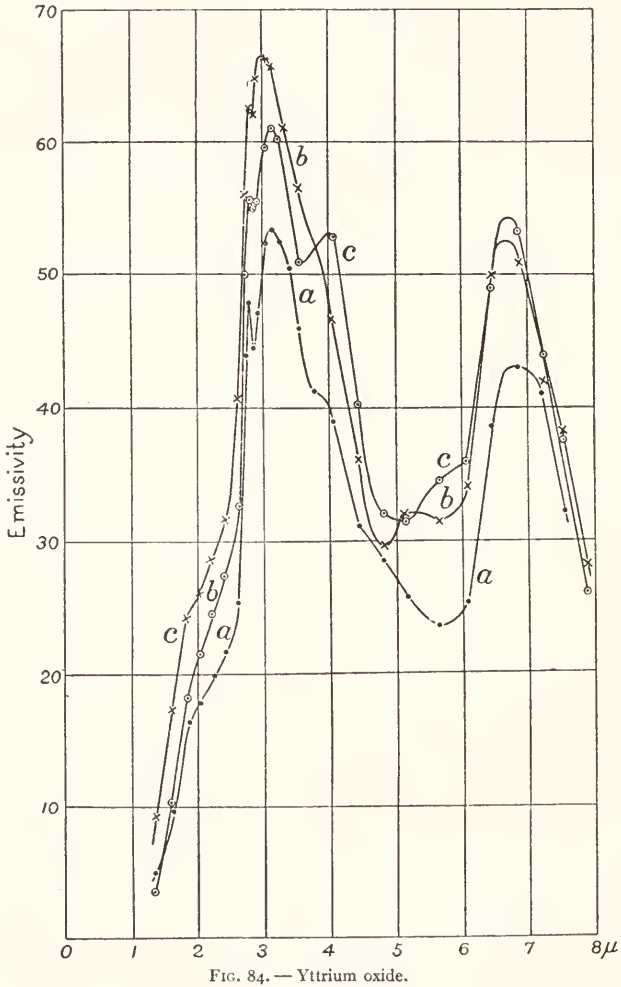

FIG. 84. — Yttrium oxide.

shown presently, in fig. 92, that this sharp band may be due to a suppression of the radiation at 6 μ, caused by a band of metallic reflection at this point. However, bands of metallic reflection are not common at these short wave-lengths, so that the maximum at 6.9 μ may be a true emission band.

In fig. 84 are shown the emission curves of three additional samples of

yttrium oxide, of unknown purity, all of which were a beautiful yellow color, as compared with the sample given in fig. 83, which was a yellowish-white. These samples were obtained by fractional precipitation from the sulphate of yttrium by means of oxalic acid. The precipitation, however, was not carried out to the extent of obtaining yttrium, erbium, and ytterbium oxides separately. In these curves the prominent bands of fig. 83, with maxima at 2 and 2.75 μ, are suppressed, and the small bands of the latter at 3 and 6.8 μ are the most prominent. These three samples were heated so that the surface appeared a dull red, the sample for curve *b* being the hottest. The emission bands occur in two groups, at 3 and 6.8 μ, respectively, just as was found in the oxides of zirconium and magnesium. There are sharp maxima at 2.8, 3.15, and 6.75 μ, and smaller bands at 2, 3.9, and 5.2 μ, respectively.

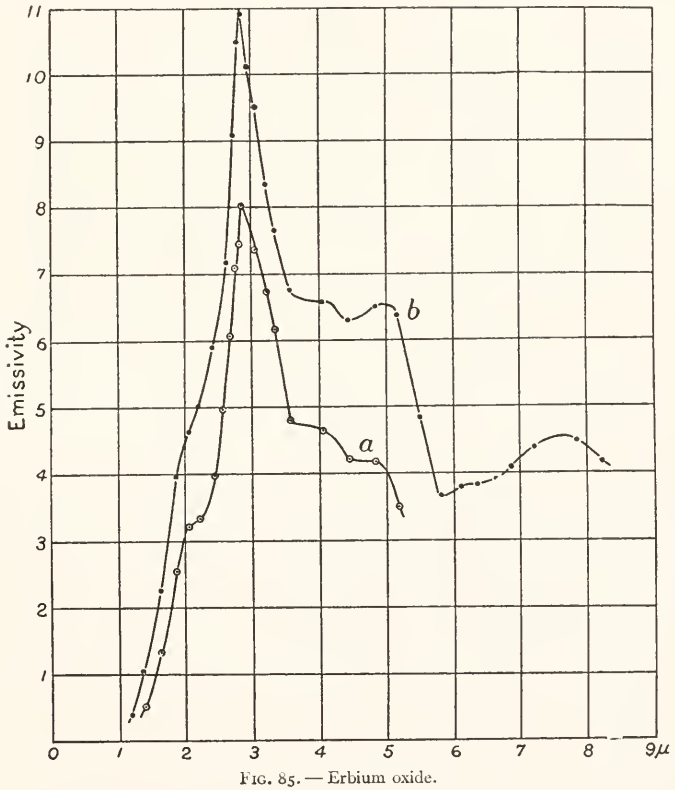

FIG. 85. — Erbium oxide.

ERBIUM OXIDE (Er_2O_3).

(Curves *a* and *b*, fig. 85.)

Curve *a* shows the emission of a layer of the oxide formed by decomposing a solution of the nitrate on a strip of platinum, heated electrically. Curve *b* gives the distribution of energy of a layer of the oxide on a heater-

tube. The two spectra are similar, with a sharp emission band at 2.85 μ. Other maxima appear at 2, 3.2, 4.1, 5, and 7.5 μ. The general outline of the spectrum is similar to that of yttrium.

NEODYMIUM OXIDE (NdO); MANGANOUS OXIDE (MnO).

(Curve *a*, NdO; curve *b*, MnO; fig. 86.)

The neodymium oxide was deposited in a thick layer upon a strip of platinum, by evaporation from a solution of the nitrate. The radiation curve shows maxima at 3, 4.4, and 4.83 μ. Beyond 6 μ the emissivity is strong and not unlike that of cerium and thorium. The scale of emissivity is one-half of the curve for MnO.

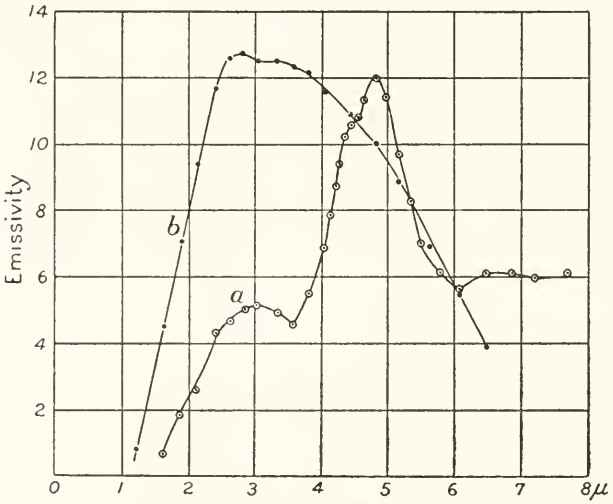

FIG. 86. — Neodymium oxide (*a*); Manganous oxide.

The manganous oxide was a grayish-brown color. The thickness of the layer upon the "heater-tube" was about 1.2 mm. The radiating surface was a dull red. The spectral radiation curve is uniformly smooth throughout its whole length, with but a slight depression at 3.2 μ to be noticed in numerous oxides. In these two curves the sensibility of the instrument is different, as is frequently the case.

ZINC OXIDE (ZnO); LEAD OXIDE (PbO).

(Curve *a*, ZnO; curve *b* and *c*, litharge (PbO), curves *e* and *f*, platinum; fig. 87.)

The zinc oxide became a yellowish-green on heating, resuming its former white color on cooling. In spite of this selective emission in the visible spectrum, the distribution of energy in the infra-red is uniform, with the usual depression at 3.2 μ. Lead oxide ("litharge") melts at a low temperature. On heating the color changes from orange to deep red. Curve *b*, fig. 87, shows the distribution of energy for the oxide after it had melted into a smooth mass and solidified. Curve *c* shows the emissivity

from an unmelted surface. The depression at 3.3 μ is marked, and at 5.5 μ there is a possible emission band. The thickness of the layer was at least 1.2 mm.

Curves *e* and *f* show the emission of a strip of platinum. No depression appears at 3.3 μ, from which it would appear that the depression at 3.3 μ is a characteristic of the oxides and not due to absorption in the instrument.

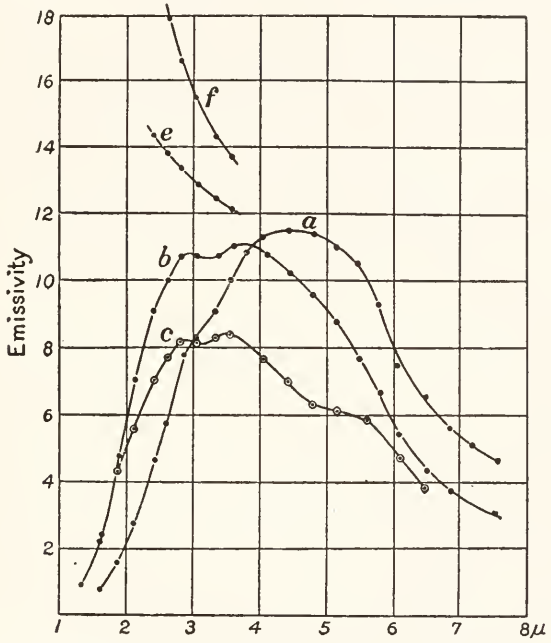

FIG. 87. — Zinc oxide (*a*); Lead oxide (*b*), (*c*); Platinum.

IRON OXIDE (Fe_2O_3); COPPER OXIDE (CuO).

(Curves *a* and *b*, Fe_2O_3; curves *c*, *d* *e*, CuO; fig. 88.)

The iron oxide used was red hematite, or "rouge." The layer on the heater-tube was 1.5 mm., heated to redness, 800°. The energy curve is smooth, except a depression at 3.2 μ. The copper-oxide layer was 1.5 mm., heated to a deep red. The energy curve is smooth, except the slight depression at 3.2 μ.

COBALT OXIDE (Co_2O_3); CHROMIUM OXIDE (Cr_2O_3); STANNIC ACID (SnO_2).

(Curve *a* = Co_2O_3; curves *b* and *c*, Cr_2O_3; curve *d*, SnO_2; fig. 89. Sensibility 80, 85, and 73, respectively. Temperature 800° to 900°).

The cobalt-oxide curve is smooth throughout, except the depression at 3 μ.

Chromium oxide is green in color, and emits a fairly smooth spectrum with a possible maximum at 5 μ. The depression at 3.2 μ is prominent.

Stannic acid is grayish-white in color, but, unlike many of the white

oxides, it emits a continuous spectrum. The depression at 3.2 μ is small. The transmission bands in cassiterite, SnO_2, were found to be small.

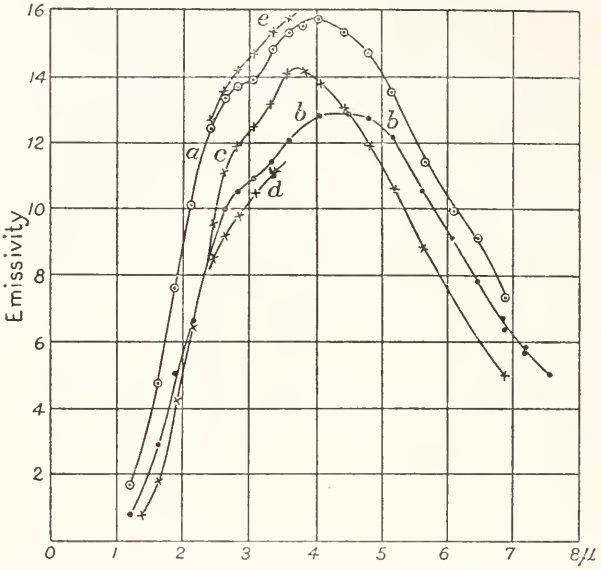

FIG. 88. — Iron oxide, (*a*) (*b*); Copper oxide.

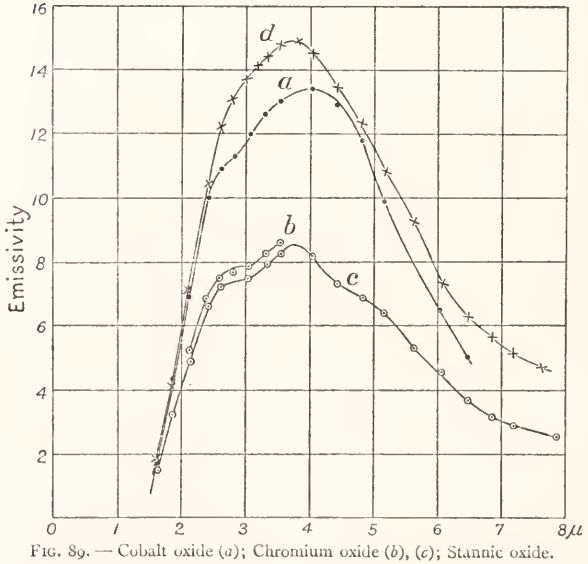

FIG. 89. — Cobalt oxide (*a*); Chromium oxide (*b*), (*c*); Stannic oxide.

NICKEL OXIDE (NiO); CALCIUM SULPHATE ($CaSO_4 + 2H_2O$).

(Curves *a*, *b*, *c* = NiO; curve *d* = $CaSO_4$; fig. 90. Temperature about 900°. Transmission, Carnegie Publication No. 65, p. 18; curve *b*, fig. 2.)

The nickel-oxide surface was rougher than for the other oxides, hence not so uniformly heated. At the highest temperature the de-

pression at 3.3 μ is very marked, while at the lower temperatures it is not so deep.

The calcium sulphate used was a thick, smooth layer of "plaster of paris," which dehydrated (at least in part) at the red heat used. The emission bands at 2, 3.2, 4.65, and 6.3 μ coincide in intensity and position with the absorption bands found in previous work (see Carnegie Publication No. 65, fig. 4). The band at 4.65 μ is shifted from its position at

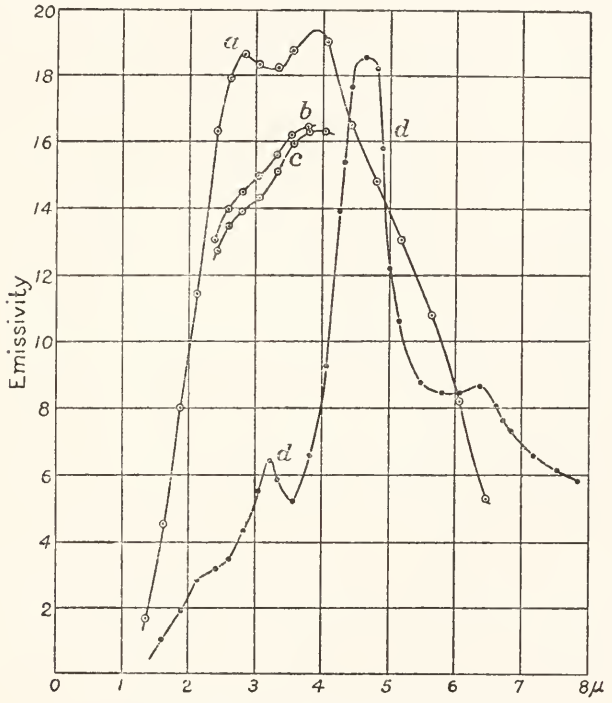

FIG. 90. — Nickel oxide (*a*), (*b*), (*c*); Calcium sulphate.

4.55 μ in anhydrite ($CaSO_4$), but coincides with the partially dehydrated selenite ($CaSO_4 + 2H_2O$) given in Carnegie Publication No. 65, figs. 3 and 4.

The absence of the band usually found at 2.8 μ may indicate that it is not due to water. Paschen found an emission band of water at 2.83 μ in the Bunsen flame.

CALCIUM OXIDE (CaO); TRICALCIUM PHOSPHATE [$Ca_3(PO_4)_2$].

(Curves *a* and *b* = CaO; curve *c* = $Ca_3(PO_4)_2$; fig. 91.)

The surfaces of these two substances were at a dull red heat. The calcium-oxide layer was somewhat cracked, but not sufficient to interfere with the radiation. The layer of oxide in each case was about 1.2 mm.

The calcium-oxide emission curve is conspicuous for its two sharp maxima, at 2.8 μ and at 4.75 μ, respectively, and a high emissivity at 8 μ,

which is not unlike that of cerium and thorium oxides, observed by Rubens. Smaller bands appear at 2.4, 3.3, and 4 μ. The calcium oxide was heated to a bright red before mounting it upon the heater-tube, and was apparently free from the carbonate (fig. 92). Since there are no emission bands belonging to that substance, it appears that the water used in making the CaO into a paste was entirely expelled.

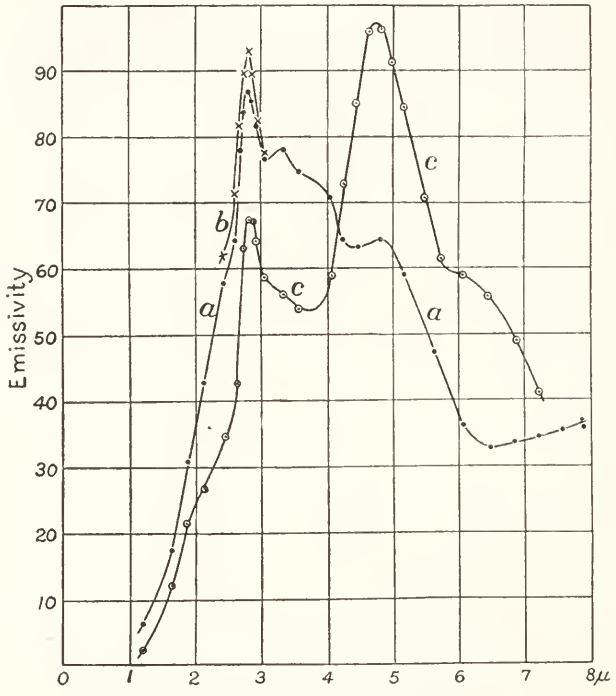

FIG. 91. — Calcium oxide (*a*); (*b*); Tricalcium phosphate.

The tricalcium phosphate has two marked emission bands, at 2.85 and 4.75 μ, respectively, and smaller bands at 2 μ and 6.2 μ. The emission spectrum is unusually similar to that of apatite (fig. 75).

A chemical analysis of calcium oxide, by Dr. H. C. P. Weber, showed no weighable amount of silica. This shows that the band at 2.8 μ is not due to silica.

CALCITE ($CaCO_3$).

(Curves *a* and *b*, fig. 92. Transmission, Carnegie Publication No. 65, p. 70.)

The sample examined was a layer of finely ground white marble. The surface color in the two cases corresponded to about 900° and 1000°, respectively. The emission curve is of interest on account of the two types of emission it contains. In the region of 6.7 μ calcite has a band of strong selective, "metallic," reflection. In this region of the spectrum the emissivity is proportional to the reflecting power, thus placing in the class with

metals. Here the emission is actually suppressed, and we have an emission minimum instead of a maximum, as will be described in the following chapter. In the remaining part of the spectrum the emission is propor-

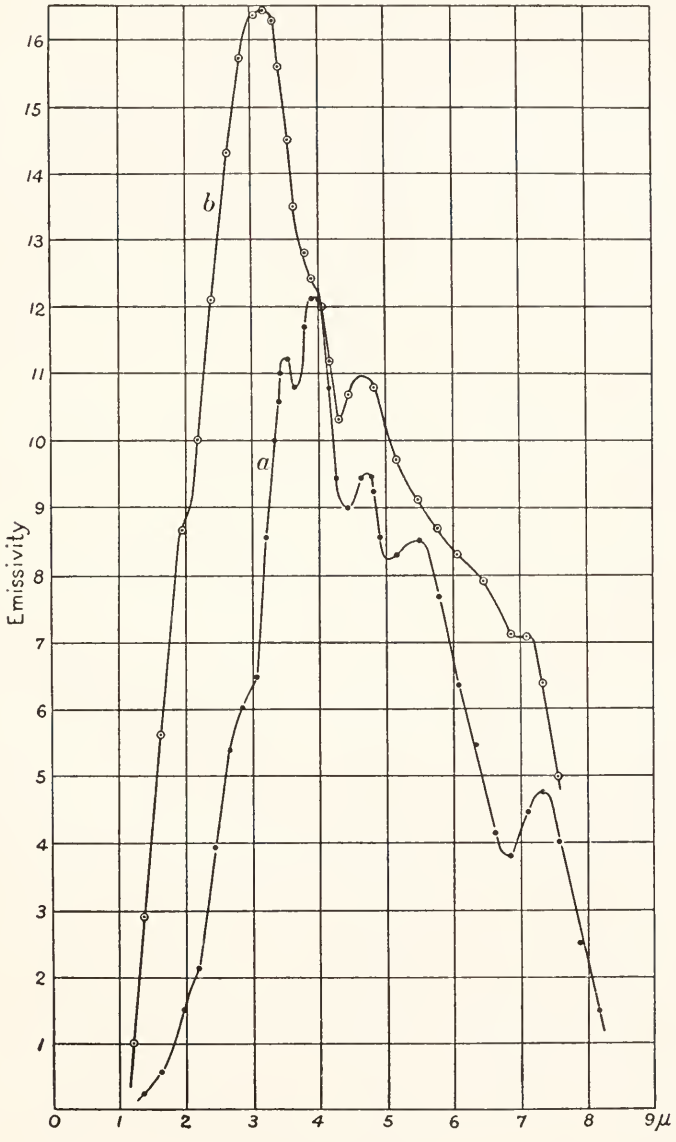

FIG. 92. — Calcite.

tional to the absorption. The emission bands at 2, 2.7, 3.5, 3.9, 4.7, and 5.5 μ coincide with the absorption bands previously observed. The apparent maximum at 7.3 μ is due to the suppression of the radiation at 6.8 μ. This fact can, of course, only be determined from a knowledge of

the reflecting power of the substance under examination. The maximum reflection and the minimum emission do not coincide on account of the high reflecting power on the side toward the long wave-lengths, which suppresses the emission curve, thus shifting its minimum farther into the infra-red. The only other example heretofore investigated is by Rosenthal,[1] for quartz, which will be described in the next chapter. The band at 4.7 μ is of interest since it occurs in CO and CO_2 in the vacuum tube radiation (see Carnegie Publication No. 35), and is in common with the *carbonates* and the *sulphates*.

RELATION BETWEEN EMISSIVITY AND ENERGY CONSUMPTION.

The substances just described must have one or both of two kinds of spectral energy distribution, due (1) to the general absorption which is present to some extent, however small, and which gives rise to a continuous spectrum, and (2) to bands of selective absorption which give rise to emission bands.

The object in examining the isochromatic radiation curves of the aforesaid solids is to determine whether or not the observed sharp emission bands behave like spectral lines, or like bands which include a considerable portion of the spectrum. If the observed bands behave like those of a gas, the emission must be proportional to the energy supplied. If the radiation is similar to the complex and highly damped emission of a solid, *e.g.* platinum, the isochromatics can not be straight lines, but must be similar to those of platinum.

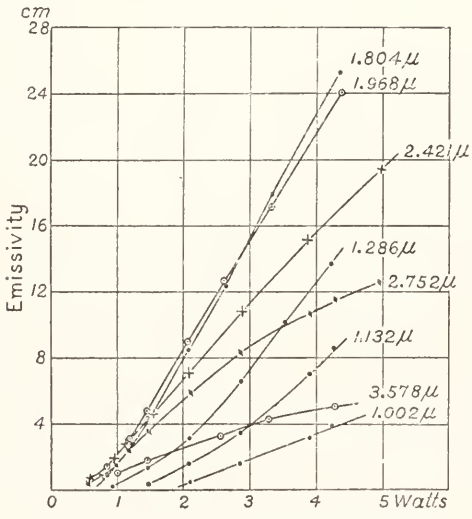

FIG. 93. — Isochromatic radiation curves of platinum.

A complete radiator emits energy, however small the amount, of all wave-lengths, whatever its temperature above the absolute zero. The isochromatic energy curves must, therefore, all begin at the origin of the energy axis; and they may have a double curvature. This is well illustrated in fig. 93 for the isochromatic radiation curve of platinum at 2.752 μ. The platinum strip was 50 by 1.5 by 0.02 mm., in an exhausted glass bulb, with a fluorite window. In this figure the graphs of wave-lengths $\lambda = 1.804\ \mu$ and $\lambda = 1.968\ \mu$ intersect at 2.8 watts, showing that the maximum of the energy curve lies between these two wave-lengths; temperature about 1100° C.

[1] Rosenthal: Ann. der Phys. (3), **68**, p. 791, 1899.

It is interesting to note that the point of inflection in the curves occurs when the isochromatic wave-length is identical with the wave-length λ_{max}, (E_{max}). This, of course, is due to the well-known property of spectral emission of a complete radiator, or a metal, in which the emissivity in the short wave-lengths increases more rapidly than on the long wave-length side of the maximum emission.

On the other hand, the graph showing the relation between the emissivity of a spectrum line and the energy supplied should intersect the energy axis at a distance from its origin, corresponding to the energy (a finite amount) required for excitation, which is different for different spectral lines. This is a well-known property of spectral lines, being independent of the wave-length.

Furthermore, if we follow the common line of reasoning (see Kayser's Spectroscopy, vol. II, pp. 59, 245, and 331) and consider the separate lines as a part of an energy curve, obtained by drawing the envelope through the highest points of the separate emission bands, then the maximum of the envelope must shift toward the short wave-lengths with increase in energy consumption, and the slant of the isochromatics must be similar to those of platinum (fig. 93). It is difficult to conceive how this is possible with discrete spectral lines which require the application of a certain amount of energy to excite them. The change of the emission curves of the Nernst glower from a discontinuous into a continuous one has already been noticed. They illustrate this envelope type of energy curve just mentioned. But it seems more probable that this is due to the rapid growth of the general emission of the intervening frequencies, which, with a doubtful broadening of the emission bands, obliterates the selective emission at high temperatures. In fig. 94 are shown the isochromatic energy curves of a Nernst glower, the values being taken from fig. 57. In fig. 95 are given a series of isochromatics for a 110-volt glower 1.4 cm. long and 1.4 mm. diameter. The current was supplied from a 2000-volt 600-watt transformer on a 110-volt circuit. The energy supply was regulated by means of resistances in the primary.

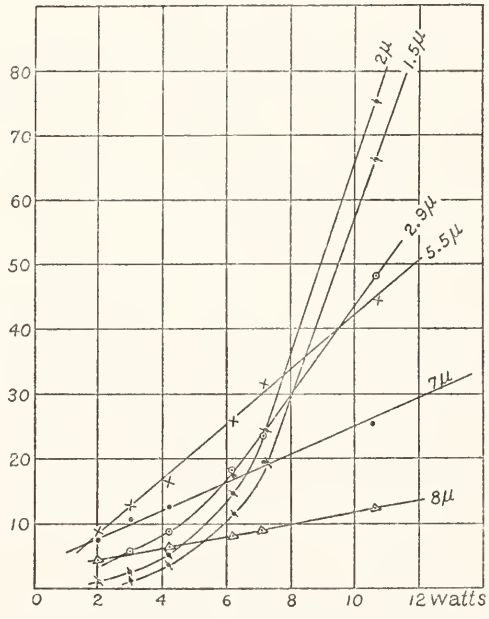

FIG. 94. — Isochromatic radiation curves of Nernst glower.

The voltage was obtained with a multiple-cell electrostatic voltmeter. The curves for the intensest part of the spectrum pass through a double curvature and have the general outline of that of platinum. The normal burning is 80 watts and above that point the isochromatics appear to

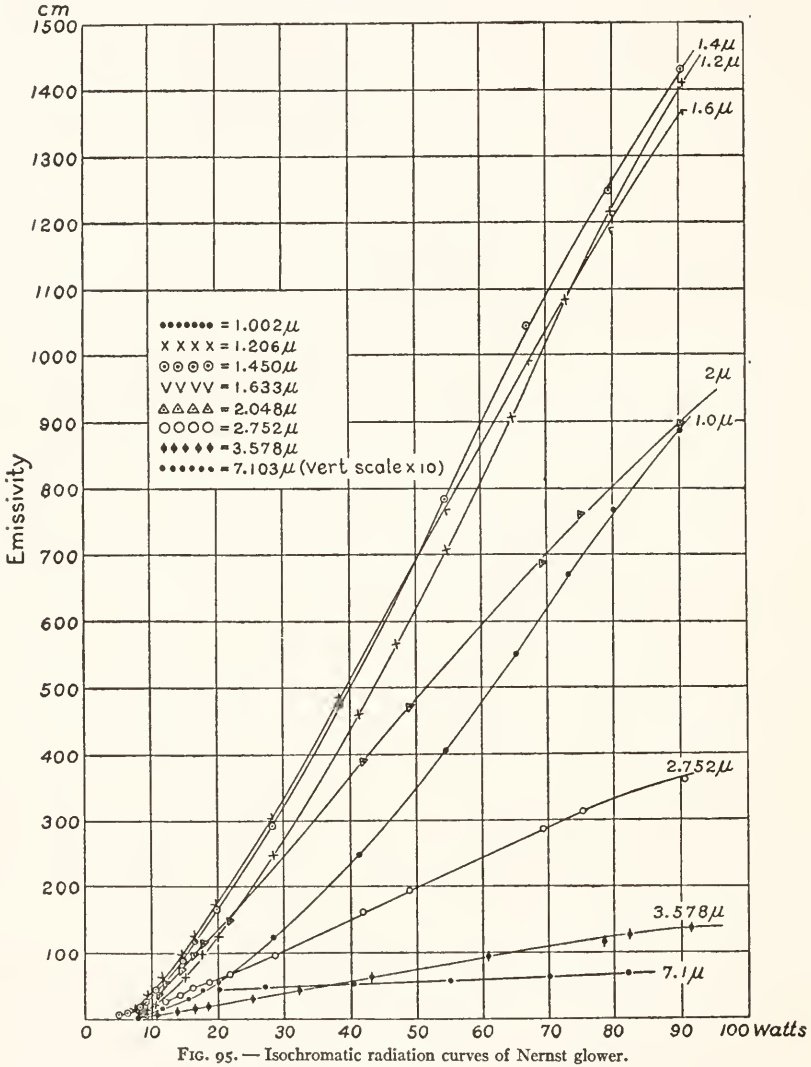

FIG. 95. — Isochromatic radiation curves of Nernst glower.

show a slight increase in curvature. The intersection of the graphs for wave-lengths $\lambda = 1.206\ \mu$ and $\lambda = 1.633\ \mu$ at 73 watts[1] shows that the maximum of the spectral energy curve for this power consumption lies between

[1] None of the isochromatics, given in this paper, have been corrected for slit-width, which would change the observed energy consumption a few per cent.

these two points, as previously observed. This method of locating the maximum eliminates the correction for slit-width, and is an independent proof of the previous observations that the maximum of the energy curve for normal burning (80 watts) can not lie at such short wave-lengths as was observed by previous investigators. This, of course, is on the assumption that the glowers were of the same material, the base of which is zirconium oxide with a small per cent of thorium or yttrium oxide.

In Carnegie Publication No. 35, p. 318, it was shown that in the case of vacuum-tube radiation the intensity of the emission lines is proportional to the energy consumption. The graphs there obtained, showing the relation between current and emissivity of a spectral emission line, are curved, due to the fact that Ohm's law does not hold for the vacuum-tube discharge. For the present examination, instruments were available to measure the energy consumption, when the graph ought to be a straight line, provided the partition of the energy emitted is in discrete lines. As a typical, selectively radiating solid, oligoclase was chosen on account of its sharp emission bands, and also on account of its homogeneity. A rod 2.5 cm. long and 2 mm. diameter was prepared in an oxyhydrogen flame. The spectrometer slit was reduced to 5 mm. in length, which permitted the entrance of radiation from only about 5 mm. of the central part of the rod, which was a perfectly clear glass, free from air-bubbles. At the highest temperatures this central part showed a peculiar faint white "luminescence" similar to the intense white noticeable in quartz when heated in the oxyhydrogen flame. The rod was thickened at the ends which seemed to prevent internal reflection of the radiation from the platinum terminals.

The distribution of energy from the central portion of this rod is shown in curve *c*, fig. 66, on 29.4 watts. The ends of the 0.3 mm. platinum terminals within the glass rod were red hot. The rod was viscous, indicating a temperature of at least 1100° to 1200°; but no light was emitted other than the hazy white glow already mentioned, which is in marked contrast with the radiation from the platinum electrodes. A similar example is given in Wood's Optics, page 457, where it is stated that sodium sulphate, in a loop of platinum wire, heated in a blast lamp, emits but little light, although the wire glows vividly.

In fig. 96 are given the isochromatic emission curves of oligoclase at wave-lengths 2.048, 2.905, 4.445, and 6.082 μ, respectively, for different values of power consumption. The graphs are for the same rod, under the same conditions of galvanometer sensibility and distance of the radiator from the silt. Two additional series of observations on different days, and using different adjustments, were made at wave-length 2.905 μ. Only one of these graphs was parallel with the one given in fig. 96, showing that there is a variation in the slant of the isochromatic curve, under different conditions. It will be noticed that, throughout the range investigated, the change in emissivity is proportional to the energy supplied, just as is true

of gases. It is possible that for some wave-lengths the thickness of the radiator was not sufficient to emit a saturated radiation, and this may explain why the emissivity at 2.048 μ apparently does not follow the same law as do the other emission bands. In order to have a displacement of the maximum of emission, just as is known for solids emitting continuous spectra, it is necessary that the intensity of the emission at the short wave-lengths increase more rapidly than it does in the long wave-lengths. The 2.048 μ isochromatic slants only a little less from the normal than does

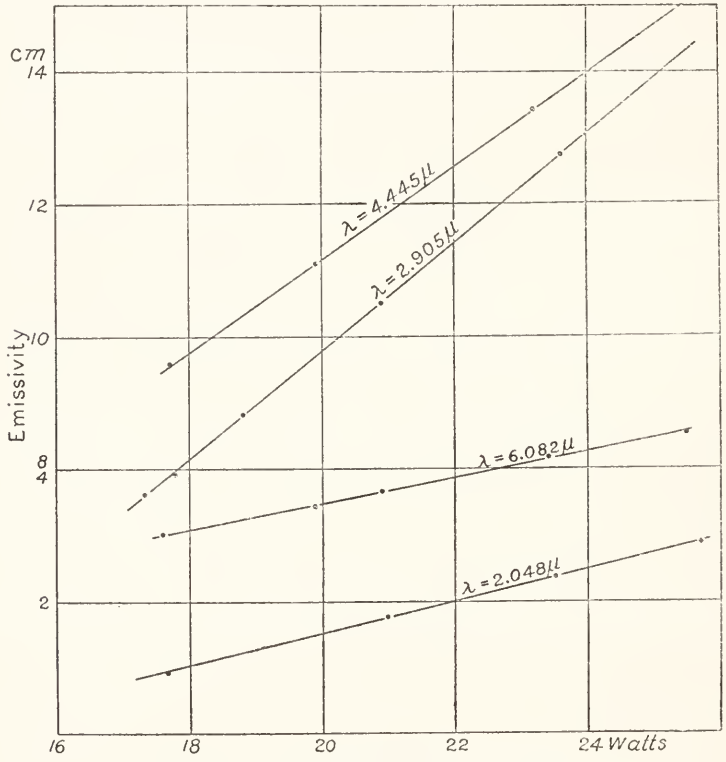

FIG. 96. — Isochromatic radiation curves of oligoclase.

$\lambda = 6.082\ \mu$. In this region of the spectrum there is a weak general absorption, while the other wave-lengths are the maxima of selective emission (absorption) bands, and it is possible that what corresponds to the emissivity constant a of a complete radiator is different for the two kinds of radiation found in this substance. It is possible that the isochromatic at 2.048 μ undergoes a sudden change, curving sharply upward, at a higher temperature. The same is true of the platinum isochromatic at 1 μ. In fact, it appears that the emissivity at 2.048 μ must suddenly change in intensity, unless oligoclase is entirely different from the other substances examined; for, like the others, in the oxyhydrogen flame, it emits an intense

white light, although, as shown in curve *c*, fig. 66, the emissivity at 2 μ is still weak when the temperature is close to the melting-point.

In oligoclase it is not possible to locate so definitely, if at all, the position of the maximum of the envelope by the intersection of the isochromatics; for the lines show no tendency to curve, as in platinum, although at closely the same temperature. By the extrapolation of the 2.9 μ and the 4.4 μ isochromatics, the intersection (obtained after correcting for slit-width) is found to be at about 8.5 watts. The maximum emission would then lie at about 3.5 μ, which is the position of the maximum of a complete radiator at 850° abs. (580° C.). On 29.4 watts, when the oligoclase was already viscous, indicating a temperature of 1100° to 1200° C. (melting-point 1300°), the maximum emission would have to lie at a much smaller wave-length than 3.5 μ, say at 2 μ, which is inconsistent with the observations that the emission curve is but little different in outline from those obtained at lower temperatures, — there being no indication of a shifting of the energy distribution. It would therefore appear that it is not permissible to consider the envelope, drawn through the emission maxima, as a criterion for judging the temperature of a substance like oligoclase. On the whole, it appears that the general emission, as distinguished from the bands of selective emission, is less intense in oligoclase than in most of the other silicates studied. Such a substance, if it would withstand high temperatures, would most nearly approach the ideal light producer. For, since the absorption coefficient is small throughout the region, to 3 μ, where, in a continuous spectrum, the greatest amount of energy is emitted, the emission spectrum would remain discontinuous, and only at the highest temperatures would the general emission become of importance, when a large amount of the energy radiated would be of wave-lengths affecting the eye.

SUMMARY.

In general, the results on the oxides furnish an excellent illustration of the shifting of the maximum of intensity of emission toward the short wave-lengths with rise in temperature, just as is known for solids emitting continuous spectra. In this respect the various emission curves of zirconium oxide are particularly conspicuous. In addition to what may be termed "general emission," in which the maximum shifts with rise in temperature, the curves of zirconium oxide are unique in having a sharp band of "selective emission" which does not shift nor broaden with rise in temperature. The results are not unlike those obtained by Anderson [1] for erbium oxide, in the visible spectrum. He found that the emission spectrum was not continuous, but consisted of bright bands superposed upon a continuous faint background. With rise in temperature the bands became more hazy in outline, and at very high temperatures the spectrum became continuous. If, according to Stark's theory, the continuous spec-

[1] Anderson: Astrophys. Jour., 26, p. 73, 1907.

trum is due to the presence of a large number of free electrons, this is to be expected. At low temperatures the electrical conductivity is small, and the emissivity is confined to particular bands caused by certain groups of electrons. With rise in temperature more electrons, extending over a wider range of wave-lengths, are excited to activity and the separate emission bands become merged into a continuous spectrum. This is not always true, however, in the present work. For example, the sharp emission band of zirconium oxide at 4.3 μ seems to retain the same intensity, superposed upon a continuous background of increasing intensity, irrespective of the temperature. In fact, many of the emission bands are as sharp as those found in gases.

Many of these oxides have an emission band in common in the region of 2.85 μ, from which it would appear that this band may be due to the oxygen atom which is in common with all of them. Furthermore, the emission spectra, when smooth, generally show a depression at 3.2 μ, for which no satisfactory explanation has been found. There are no atmospheric absorption bands in this region, and fluorite is not known (see fig. 29) to have absorption bands at this point (Paschen's absorption curve for a 4 mm. plate shows an increase in absorption of 2 per cent from 2.75 to 3.2 μ, maximum at about 3.1 μ). The emission spectrum of platinum, carefully examined at the same time, showed no depression. The emission curve of the bare "heater-tube," which consists of a porcelain tube wound with fine platinum wire, likewise gave a smooth emission curve similar to that of the platinum strip. On the whole, the present data indicate that the depression is a characteristic of the oxides. In other words, the oxides have a small (sometimes large) characteristic emission band at $\lambda=2.8$ to $\lambda=3$ μ and a second group of bands at 4.5 to 5 μ. If this be true, then it will be necessary to assign the cause of the selective emission to the element common to all the oxides, viz, to oxygen. It is well known that groups of atoms have characteristic bands; but, heretofore, no data has been at hand which, in any way, indicated the possibility of the characteristic bands being due to a particular atom in the group.

The tentative conclusion that these emission bands in the oxides are due to oxygen atoms is perhaps to be expected, for the presence of traces of the universal impurity, silica, will not explain matters. The oxides are the most important and the most stable of all the important groups of chemical compounds; and the spectra of substances belonging to a particular group are similar. But few substances are inert to the action of oxygen. The spectrum of oxygen (see Carnegie Publication No. 35, p. 49) shows absorption bands at 3.2 and 4.75 μ. The emission spectra of CO and CO_2 show bands in the region of 2.7 and 4.75 μ (Carnegie Publication No. 35, p. 313). Oxygen in a vacuum-tube showed a strong emission band at 4.75 μ, which, at the time the research was made, was ascribed to CO or CO_2 supposed to be formed by the electrical discharge. In view of the

fact that, with rise in temperature, the CO_2 emission band shifts toward that of CO, at 4.6 μ, and that eventually all three gases, CO_2, CO, and O, when radiating by electrical excitation in a vacuum-tube, have their important emission band in common at 4.75 μ, it does not seem unreasonable to assume that the latter maximum is due to the oxygen atom set free during the time intervening between dissociation and recombination, brought about by the electrical discharge in the carbon oxides.

In a broad sense the intensity and sharpness of the emission bands are a function of the electrical conductivity. The best insulators (strong bases), *e.g.*, the refractory silicates, the oxides of aluminium, zirconium, erbium, etc., have the sharpest emission bands, while the best electrical conductors, such as the oxides of cerium, iron, zinc, etc., have no sharp emission bands. The molecular weight of the base seems to affect the sharpness of the bands to as great an extent as does the electrical conductivity, the sharpest bands occurring as a rule in oxides of low basic molecular weight. These results, if true, are to be expected from our knowledge of the emission, absorption, and reflection of electrical conductors and insulators.[1]

Paschen, using the spectral energy curves of the oxides of iron and copper, found no variation of the emissivity constant, a, with rise in temperature. On the other hand, Lummer and Pringsheim, using the total radiation from these substances, found that the emissivity increased with rise in temperature. Such a change in emissivity is to be expected, for it can be shown that at the highest temperatures the emissivity constant, a, must decrease, otherwise a point would be reached where the emissivity is greater than that of a complete radiator. In the present curves, where sometimes at high temperatures the emission seems to be distributed into apparently two bands, the "constant" a, derived from the spectral energy curve of one band, may be different from that obtained from the total radiation measurements. This is illustrated in the present study of the Nernst glower, where Mendenhall and Ingersoll,[2] using total radiation, found no certain variation in a with rise in temperature.

From one line of theoretical consideration, one might expect to find, with rise in temperature and the accompanying increase in the electrical conductivity of the oxides, that the reflecting power increases. If this be true, then the spectral emission ought to become more continuous, as is found in the Nernst glower, and the emissivity constant, a, should retain a high value similar to that of metallic electrical conductors. The value of a from the spectral radiation curve was found to decrease with rise in temperature, while Mendenhall and Ingersoll found no certain variation in a, when measuring the total radiation. It is evident that experiments

[1] This subject has been thoroughly treated by Aschkinass: Ann. der Phys. (4), **17**, p. 960, 1905.

[2] Mendenhall & Ingersoll: Phys. Rev., **24**, p. 230, 1907; **25**, p. 1, 1907.

on the reflecting power of oxides at high temperatures will be necessary. The emissivity of the sharp spectral lines in a magnetic field will also require examination, although, on account of the wave-lengths involved, the possibility of obtaining results is not promising.

It may be added that the well-defined maxima of emission are not affected by change in temperature, which is in marked contrast with the results of Königsberger[1] for the limited region of the visible spectrum. Whether the emission maxima at 2.85 μ and 4.75 μ are due to the presence of water, in the various minerals, remains to be determined. If they are due to water, then one would expect to find them in calcium sulphate ($CaSO_4+2H_2O$), as well as in calcium oxide (CaO; probably some CaOH). But in the sulphate no band was found at 2.9 μ, where the emission should be the most intense if due to water. The band at 4.75 μ is characteristic of the sulphates (see Carnegie Publication No. 65). On the whole, the assumption that these bands are due to the presence of water is no more satisfactory than to ascribe them to the common constituent, viz, oxygen.

The isochromatics of oligoclase show that the emissivity is proportional to the energy in-put, thus differing from the other solids investigated; but, in view of the fact that in the oxyhydrogen flame the oligoclase emits an intensely white light, it appears that the emissivity must suddenly undergo a change in the visible spectrum, and perhaps form a more continuous spectrum in the infra-red.

In considering the emissivity of these oxides in connection with the radiation from the sun which is a mixture of these substances in various conditions of temperature and physical state, and remembering that the tendency of the solids is to emit a continuous spectrum at high temperatures, it forms an interesting field for speculation as to what one ought to expect for the composite radiation from the solar surface. The available data show that gases radiating in a vacuum-tube and the metallic vapors in the arc have their strongest emission lines in the region of 1 μ. In the spark discharge the metallic vapors appear to have their maximum energy in the ultra-violet. With data provided by the Astrophysical Observatory (see vol. 2 of the Annals), giving the distribution of energy in the normal solar spectrum, it has not been possible for me to compute a consistent λ_{max} for different wave-lengths, nor a uniform value of the radiation constant a (the value of a varied from 21.9 at 0.4 μ, 15.6 at 0.5 μ, 11.0 at 0.6 μ, 7.8 at 0.7 μ to 5.4 at 1.2 μ), by the methods given on a previous page, and it seems evident that these laws are not applicable. If, as the data herewith presented on the emissivity of the oxides seems to show (assuming the solar surface to be solid, electrolytic conductor as compared with a pure metal with high reflecting power) these radiation laws do not hold, how much less must they be true in the case of the solar surface in its real condition.

[1] Königsberger: Ann. der Phys. (4), 4, p. 796, 1901.

CHAPTER III.

RADIATION FROM SELECTIVELY REFLECTING BODIES, WITH SPECIAL REFERENCE TO THE MOON.

In Carnegie Publication No. 65, p. 110, on infra-red reflection spectra,[1] the writer showed that all the silicates examined have a region of strong selective reflection in the region of 8 to 10 μ and discussed the effect this would have upon a reflecting surface like the earth, or the moon, which is composed largely of silicates. Since this discussion has brought forth comments favorable and unfavorable, in print and in private communications, the purpose of the present paper is to summarize, in a general way, the present data bearing upon the subject, and to discuss certain points not mentioned in the previous communication. The computed temperatures of the sun and of the moon derived in the present paper will be used in the subsequent calculations, which will be found to be in slight disagreement with the writer's previous results. As a whole, it will be shown how easy it is to obtain estimated values which ultimately can have but little meaning other than a guide in experimental work.

THE EFFECTIVE TEMPERATURE OF THE SUN.

It has been shown by Poynting[2] that, when a surface is a complete radiator and absorber, its temperature can be determined at once by the fourth power law, if we know the rate at which it is radiating energy. If it radiates what it receives from the sun, then a knowledge of the solar constant enables us to find the temperature, which will be the highest the surface can attain when it is receiving heat only from the sun. Knowing the solar constant and the radiation constant ($\sigma = 5.32 \times 10^{-5}$ ergs Kurlbaum)[3] Poynting computes the effective temperature of the sun. If s is the radius of the sun's surface, R is the radiation per square centimeter; then the total rate of emission is $4\pi s^2 R$. This must equal the radiation passing through the sphere of radius r, at the distance of the earth, and with a surface $4\pi r^2$ gives

$$4\pi s^2 R = 4\pi r^2 S$$

where S is the solar constant. Hence $R = 46000\ S$. Using the solar

[1] Investigations of Infra-red Spectra, Parts III and IV, published by the Carnegie Institution of Washington, D. C., December, 1906.

[2] Phil. Trans. Roy. Soc. Lond., vol. 202 A, p. 525, 1903.

[3] Kurlbaum: Wied. Ann., 65, p. 748, 1898.

constant $S=2.5$ gram calories per minute$=0.175\times10^7$ ergs per square centimeter per second, $R=0.805\times10^{11}$ ergs.

If we equate the sun's radiation to $\sigma\theta^4$, where σ is the radiation constant, we get θ, the "effective temperature" of the sun, that is, the temperature of a full radiator which is emitting energy at the same rate.

Thus, $5.35\times10^{-5}\ \theta^4=0.805\times10^{11}$; whence $\theta=6200°$ abs.

With each new determination, however, the solar constant is being reduced from the former high value, so that a more probable value[1] is about 2.1 gram calories per square centimeter per minute.

Using this value of $S=2.1=0.147\times10^7$ ergs per square centimeter per second,

$$R=0.0676\times10^{11},$$

whence

$$\theta=5980°\text{ abs.}$$

This is somewhat closer to Wilson's[2] value (5773° abs.), which he obtained by making a direct comparison of the radiation from the sun with that from a "full radiator" [3] at a known temperature.

Warburg[4] has also computed the probable temperature of the sun. He assumes that the rate of radiation per degree is constant, and that the Stefan-Boltzmann law is applicable at all temperatures. For $S=2.54$ gram calories per second, the computed temperature is 6256° abs., and for $S=2.17$ gram calories per second, a temperature of 6014° abs.

Fery and Millochau[5] have measured the temperature of the solar surface with a pyrometer. The mean value of the observed temperature, after correcting for atmospheric absorption, is 5620° abs. For different parts of the solar disk the temperatures vary from 5888° to 5963° abs.

Abbot (*loc. cit.*) gives a solar spectrum energy curve, deduced from bolometric measurements, in which the maximum occurs at 0.49 μ, with a possibility of the maximum[6] lying at about $\lambda=0.46\ \mu$. The equation $\lambda_{max}\ T=\text{const.}=2920$, using the value of $\lambda=0.46\ \mu$, gives a black-body

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[1] Abbot: Smithsonian Miscellaneous Collections, vol. **45**, p. 81, 1903. See also his later results, Annals Astrophys. Obs., vol. **2**, p. 99.

[2] Wilson: Proc. Roy. Soc., vol. **69**, p. 312, 1901.

[3] Poynting (loc. cit.) very aptly says: "A surface which absorbs and therefore emits every kind of radiation, is usually described as 'black', a description which is obviously bad when the surface is luminous. It is much better described as 'a full absorber' or 'a full radiator,'" *i.e.*, a complete radiator, as distinguished from a partial radiator or so-called "non-black body." In justice to Kirchhoff who was the first to give a clear discussion of this subject, it should be called the *Kirchhoff radiator*.

[4] Warburg: Verb. Deutsch. Phys. Ges., **1**, p. 50, 1899.

[5] Fery & Millochau: C. R., **143**, pp. 505, 570, 731, 1906.

[6] The curve as drawn by Abbot is very asymmetrical and depressed on the side of the short wave-length. From the data given, it is possible to draw the radiation curve more symmetrical, as one would expect it to be, which shifts the maximum to about 0.46 μ. See also his later results, Annals Astrophys. Obs., vol. **2**, which have been published since writing this paper.

temperature of about 6300° abs. One of the most refractory substances farthest removed from a full radiator in its emissive power is bright platinum. For this substance the constant is 2630 instead of 2920. If the radiation from the sun is purely thermal it must lie between the "black body" and bright platinum in its radiating properties.

If the sun radiates like platinum, from the equation

$$\lambda_{max} T = 2630, \text{ using } \lambda_{max} = 0.46\ \mu \qquad T = 5700° \text{ abs.}$$

The value of the sun's temperature, viz, 5900°, used in the present computations, is about the mean of the "observed" and the computed temperatures. From the results given in the preceding chapter, it is evident that the true temperature of the sun can not be determined by these methods.

THE LIMITING TEMPERATURE OF THE SURFACE OF THE MOON.

Poynting (*loc. cit.*) further shows that when there is no conduction inwards from the surface, the highest temperature of a full radiator is attained when its radiation is equal to the energy received. Equating the energy to the solar constant, using $S = 0.175 \times 10^7$ ergs

$$5.35 \times 10^{-5} \theta^4 = 0.175 \times 10^7$$

whence

$$\theta = 426° \text{ abs.}$$

which is the upper limit of the temperature of the moon, assuming that it absorbs all the energy received from the sun. If part of the energy is reflected and only a fraction x of that falling on it is absorbed, then the effective lunar temperature is $426\sqrt[4]{x}$ abs. From Langley's[1] estimate that the moon absorbs $x = \frac{7}{8}$ the energy it receives, Poynting (*loc. cit.*) computes the upper limit of temperature of the surface exposed to a zenith sun to be

$$\theta = 426 \times (\tfrac{7}{8})^{\frac{1}{4}} = 412° \text{ abs.}$$

But this upper limit to the temperature of the hottest part of an airless planet is never attained because the moon turns the same face to the earth instead of to the sun. He shows that, if N is the normal stream of radiation from a unit of surface of the moon immediately under the sun, the normal stream from the equivalent flat disk is $Nd = \frac{2}{3}N$.

"The effective temperature of the flat disk is therefore $\sqrt[4]{\frac{2}{3}}$ that of the surface immediately under the sun at the same distance from it. Then the effective average temperature is $412 \times \sqrt[4]{\frac{2}{3}} = 371°$ abs. The upper limit then, to the average effective temperature of the moon's disk, is just below that of boiling water."

If we use $S = 0.147 \times 10^7$ instead of 0.175×10^7, $\theta = 408°$ abs. and the "effective average temperature" is $408\sqrt[4]{\frac{2}{3} \cdot \frac{7}{8}} = 350°$ abs. or 82° C. for the full moon. This assumes no conduction inwards. Evidently there

[1] Langley: Nat. Acad. Sci., vol. 4, part. 2, p. 197.

is some heat conducted inwards, for the results of Langley (*loc. cit.*) show[1] that the surface of the full moon is about 300° abs.

FALL OF TEMPERATURE OF THE MOON DURING ECLIPSE.

As already mentioned in Carnegie Publication No. 65, page 110, Langley made observations on the eclipse of the sun on September 23, 1885, which indicate a sudden and very rapid fall of energy received from the moon at the beginning of the eclipse, with some indications of a rise nearly as rapid after its conclusion. In Carnegie Publication No. 65, page 113, are plotted his observed galvanometer deflections during the progress of the eclipse. The observations were interrupted by the formation of clouds just at the predicted time for the moon to leave the umbra. The curve shows that in the short time of about 1.5 hours, in passing from the penumbra to the umbra, the radiation from the west limb has fallen from a maximum to a zero value. In other words, the fall of temperature is practically coincident with the change in illumination, and at first appeared to the writer[2] to indicate that the greater part of the observed energy is due to reflection. That the moon at mid-eclipse is still as warm as the earth is shown by the fact that the galvanometer gave zero (or only small positive) deflections. If the moon had been cooler than the earth, then the deflections would have been negative. Subsequent search of the literature on the subject shows that Very[3] found appreciable radiation from the moon during totality. The following computations show that this is to be expected. After about 11 days of insolation the temperature of the sun-lit surface of the moon will be fairly constant. From the surface inwards there will be a layer which may be considered at a uniform temperature for the period of 1.5 hours, as compared with 11 days. If, then, the moon were suddenly eclipsed, the fall of temperature of the surface with time ($x=0$, $\theta=f(t)$; assuming at time $t=0$, that $\theta_0=300°$ abs.) is found from the equation

$$k\frac{d^2\theta}{dx^2}-\sigma\theta^4=ds\frac{d\theta}{dt}$$

where k=conductivity, d=density, and s=specific heat. The first term in the equation represents the energy lost by conduction (it is assumed

[1] Very, Astrophys. Jour., 8, pp. 273 and 274, 1898, however, records "inferred effective temperatures" as high as 455° abs. for limited regions of the moon, and (loc. cit., p. 286) a mean surface temperature of +97° C. The fact that the moon absorbs energy from the sun (the maximum of which is of short wave-lengths) and emits energy of wave-lengths from 8 to 10 μ, where, on account of the probable high reflecting power, the emissivity is very low, would explain why Mr. Very has found a temperature which is much higher than that of a complete radiator under similar conditions.

[2] Phys. Rev., 23, p. 247, 1906.

[3] Very: Prize Essay on the Distribution of the Moon's Heat, p. 40. Professor Very has called my attention to an error in Carnegie Publication No. 65, p. 112, third line from the top: viz, "Harrison (not Langley) reminds the reader . . ."

that there is conduction in only one direction, hence the differential terms in y and z disappear). The second term represents the loss of heat by radiation from the surface; while the last term represents the change in temperature at the surface. The dependent variable enters here as a fourth power, and makes the solution difficult. The computations are made for instantaneous eclipse, while in the actual case the shadow moves slowly across the surafce. Hence the error due to neglecting conductivity is partly compensated by the slow eclipse.

By neglecting conductivity from the interior, the temperature of the surface will fall more rapidly and we have a steeper temperature decadence curve. The solution of the equation is very simple if we neglect conduction, and is

$$\theta = \frac{\theta_0}{\sqrt[3]{\frac{3\theta_0^3 \sigma t}{ds} + 1}}$$

for t in minutes, $\sigma = 76.6 \times 10^{-12}$ gram calories per square centimeter per minute, $d = 2$, and $s = 0.2$ (approximate values for rock material). Hence

$$\theta = \frac{300^\circ}{\sqrt[3]{1 + 0.0155t}}$$

In fig. 97 are plotted the temperature decadence curves for the radiation constant σ, for 0.3 σ (emissivity of iron oxide) and for 0.1 σ. The curves show that for a full radiator the temperature would fall from 300° to 280° (room temperature when the bolometer would be in temperature equilibrium with the moon) in 17 minutes, for 0.3 σ in 55 minutes, and for 0.1 σ in 140 minutes. The solution for 0.1 σ and 0.3 σ is, of course, only approximate since the emissivity varies more nearly as the fifth power instead of the fourth power, as here used; and the computed temperatures should be somewhat higher. The computation is also made (fig. 97), assuming the temperature to be 350°. Here, for a complete radiator the temperature would fall from 350° to 280° in 38 minutes, and for 0.3 σ in about 130 minutes. By including the conductivity term these periods would be considerably prolonged. The present solution is close enough, however, to show that the temperature (300°) decadence curve is not coincident with the eclipse curve, unless the emissivity is of the order 0.3 σ. Hence the writer's[1] previous surmise that at the beginning of totality radiation should still be appreciable is substantiated, although the observations made by Langley seemed to contradict it. Very's observations[2] show that during totality of the eclipse of January 17, 1889, the radiation from the umbra of the eclipsed moon was about 1 per cent of the heat which was to be

[1] Phys. Rev., **23**, p. 247, 1906.

[2] Very: Distribution of the Moon's Heat, p. 40.

expected from the full moon. Boeddicker[1] also records that the minimum of the heat-effect falls decidedly later than the minimum illumination.

REFLECTION AND RADIATION FROM THE MOON.

Using the data just computed, we are now in a position to make a rough comparison of the relative amounts of energy reflected by and radiated from the moon. In the short wave-lengths the reflecting power depends upon the refractive index, while at 8 to 10 μ the reflecting power will depend upon the refractive index and the extinction coefficient (see Drude's Optics, p. 336), and at all times will have a high value, except at 7 μ. The reflecting power of the moon is variously recorded[2] from 0.09 to 0.23, which values are several times higher than the refractive index of ordinary rocks permits. This seems to indicate internal reflection.

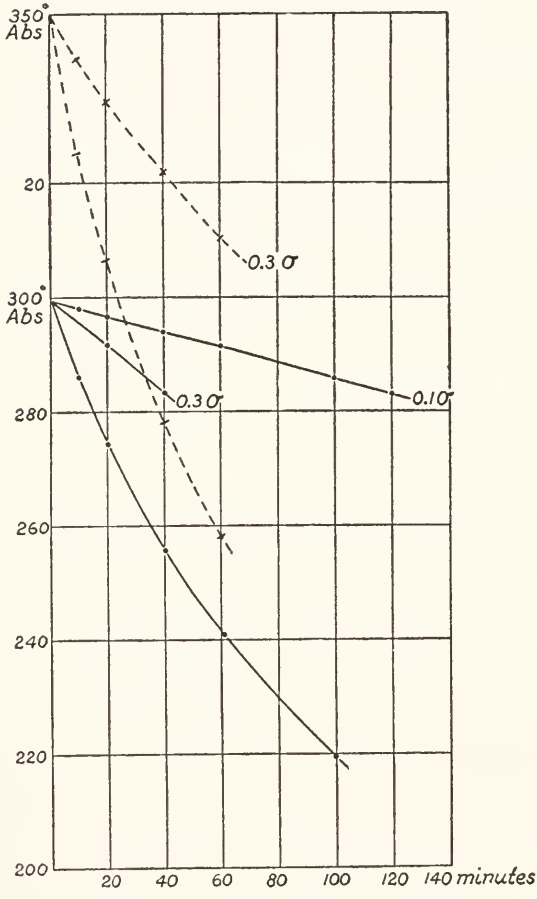

FIG. 97. — Lunar temperature decadence during eclipse.

The question is therefore reduced to finding the ratio of the energy emitted by the moon to the energy of the sun, reflected from the lunar surface. For this purpose the temperatures of the moon and of the sun (350° abs. and 5900° abs., respectively) given on the preceding pages are employed. The values are taken slightly lower, although it makes but slight difference in the final computation. We are not so much concerned with the question as to where the maximum emission of the moon occurs as we are in the fact that, in the region of 8 to 10 μ, where Langley observed radiation from the moon, there is also reflected energy from the sun. From the transmis-

[1] Boeddicker: Trans. Roy. Dublin Soc., **3**, p. 321, 1885.
[2] Very: Astrophysical Jour., **8**, p. 276, etc., 1898.

sion curves of the water vapor (curve *c*, fig. 102) it will be seen that in the region from 5 to 8 μ nearly all the energy will be absorbed by the earth's atmosphere. The reflecting power of the moon for visible rays, according to Langley (*loc. cit.*), is only $\frac{1}{500000}$ full sunlight. Assuming that at 9 μ the reflecting power of the silicates is, on an average, 10 times that at 0.5 to 4 μ, this value becomes $\frac{1}{50000}$ or 0.00002. (This seems a fair estimate of ratio of the reflecting power of the silicates at 1 and 9 μ. In the absence of better data this solution can be only a rough approximation.)

Using the above values for the temperature of the moon and of the sun, from Planck's[1] formula for the distribution of the energy in the spectrum of a complete radiator (which, of course, the moon is not)

$$E_\lambda = c_1\lambda^{-5}(e^{c_2/\lambda T} - 1)^{-1}$$

we can obtain the ratio of the intensities for the two temperatures $T = 350°$ abs. and $T_2 = 5900°$ abs. from the formula

$$(e^{c_2/\lambda T_2} - 1) \div (e^{c_2/\lambda T_1} - 1)$$

Where $c_2 = 14{,}500$ and $\lambda = 9\ \mu$. The ratio is 0.00316. But the moon, not being a perfect radiator, will have a smaller emissivity at 8 to 10 μ. If its surface were iron oxide,[2] its emissivity would be only 0.3 that of a full radiator, and, for the region at 9 μ, judging from the drop in the emission curve (see Carnegie Publication No. 65, p. 111) and the high reflecting power of the silicates, the emissive power may be less than this, say 0.1. This ratio of the emissive power of the moon to that of the sun will then be 0.000316, which is 16 times (0.000316 ÷ 0.00002) the reflected energy of the sun from the moon. If we had taken 300° as the temperature of the moon, then this ratio would be (0.00014 ÷ 0.00002) = 7 instead of 16. Computations[3] like these, which require all sorts of assumptions, can be of little value ultimately. Any computation can not be more than a rough approximation, for the reflecting powers, observed up to 4 μ, will be too high, due to internal reflection. In the region of 8 to 10 μ (for silicates) there can be but little if any internal reflection. Hence, the ratios just obtained are too low, but how much so is difficult to estimate because of the lack of data. We know that Langley observed also direct radiation from the sun, in this region of the spectrum, and from existing data of the radiation from the moon in this region we do not know how much of it is selectively reflected energy from the sun. The amount reflected must be small, but, since the total amount emitted is also small, it is important to establish the fact that there is selective reflection in this region.

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[1] Planck: Verb. Deutsch. Phys. Ges., **2**, p. 202, 1900.

[2] Kayser: Spectroscopy, vol. **2**, p. 80.

[3] Very: Astrophys. Jour., **24**, p. 353, 1906, computes a much greater difference between the amount reflected and the amount emitted.

EMISSION FROM A PARTIAL RADIATOR.

We have now to consider a problem which has heretofore not been discussed in connection with the radiation from the moon. Planck's formula for the intensity of radiation at a given wave-length λ in the spectrum of a complete radiator is

$$E_\lambda = c_1 \lambda^{-5} (e^{c_2/\lambda T} - 1)^{-1}$$

For any radiating body the emission $\phi_\lambda = A_\lambda E_\lambda$, where A is the absorption coefficient. But $A_\lambda = 1 - R_\lambda$ (for "transparent media," *i.e.*, non-metals), where R is the reflecting power, and hence $\phi_\lambda = E_\lambda (1 - R_\lambda)$.

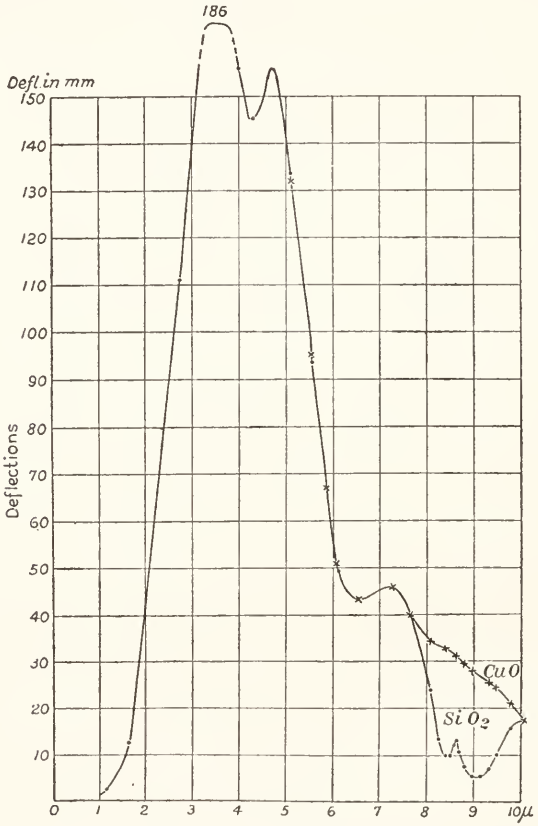

FIG. 98. — Emission spectrum of copper oxide and of quartz, 325° C. (Rosenthal).

It follows therefore that a selectively reflecting body like quartz will be a partial radiator[1] and that if we compare its radiation curves with that of a complete radiator, there will be *minima* of *emission* in the region

[1] Partial radiators may be divided into so-called "gray bodies" and bodies having a highly selective emission. Quartz belongs to the latter class.

of 8.5 and 9.03 μ. This was predicted by Aschkinass[1] and experimentally verified by Rosenthal,[2] with quartz, mica, and glass (see fig. 98). The latter found the observed emission curves of these substances to coincide precisely with the computed curves, using the observed reflecting power of these minerals and the observed emission curve of a full radiator at the same temperature.

Since we have constantly before us examples of selective emission, such as the Welsbach mantle, and high temperature radiation of such metals as tungsten and tantalum, in the visible spectrum, it will be of interest to consider the radiation of several substances having bands of selective reflection in the infra-red. In fig. 99 is given an illustration of the marked effect of selective reflection upon emission. The extraordinary reflection of carborundum (SiC) has been found in only one other substance, viz,

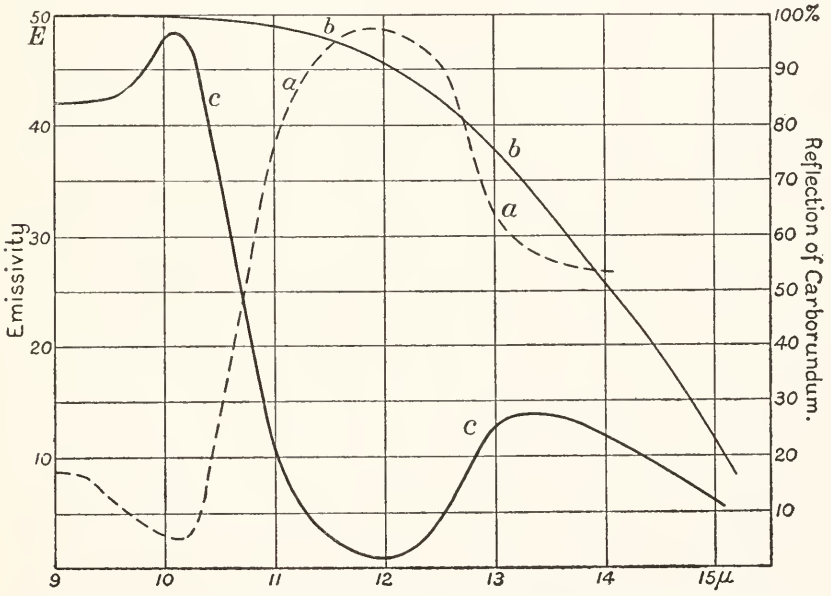

FIG. 99. — Reflection from carborundum (*a*); Radiation of complete radiator at 300° abs. (*b*); Radiation from carborundum at 300° abs. (*c*).

quartz, and in the latter it is the result of two well-defined bands, at 8.5 and 9.03 μ. The effect of such a band on the dispersion of this substance must be very marked. In fact, the unusual dispersion in the visible spectrum found by others no doubt is greatly influenced by this band. In this figure are given the computed energy curve for a perfect radiator (using Planck's formula — any temperature might have been selected instead of 300° abs.) and the computed energy curve of carborundum at the same

[1] Aschkinass: Verb. d. Deutsch. Phys. Ges., **17**, p. 101, 1898.

[2] Rosenthal: Ann. der Phys. (3), **68**, p. 791, 1899.

temperature, using the formula $\phi_\lambda = E_\lambda(1 - R_\lambda)$, where R is the observed reflecting power and E is the corresponding intensity of the full radiator. It will be noticed that the radiation will be highly selective, and that at 10 μ it approaches closely to that of the complete radiator. If, then, one were to observe the emission curve of carborundum, the maximum at 10 μ would appear as an "emission band," but its explanation is different from that of emission bands of hot vapors, *e.g.*, CO_2 and H_2O in the Bunsen flame. In fig. 100 is given the observed reflection curve, *a*, of quartz, and the computed emission curves of a complete radiator, *b*, and of quartz, *c*, at a temperature of 400° abs.

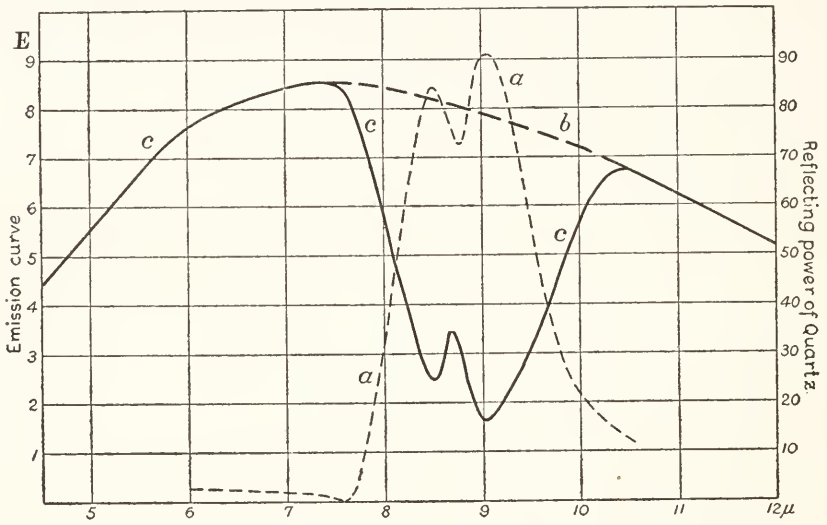

FIG. 100. — Reflecting power of quartz (*a*); Emission of complete radiator at 400° abs. (*b*); Emission curve (*c*) of quartz at 400° abs.

In fig. 101 are given the computed emission curves, *a* and *b*, for a complete radiator, for temperatures 300° and 400° abs., respectively, and the corresponding emission curves, *c* and *d*, of quartz, at the same temperature using the values of the reflecting power of quartz given by Rosenthal (*loc. cit.*). These values are somewhat lower than found by the writer. In general, the difference in the emissivity of the silicates and that of a full radiator at 8 to 10 μ would not be so marked as in quartz. For mica (see Carnegie Publication No. 65) the emission minima would occur at 9.1 and 9.8 μ, while for granite the emission minimum would extend from 8.5 to 10 μ. The combination would have an appreciable effect upon the radiation curve of a surface like that of the moon. Even, if we exclude atmospheric absorption, the emission curve (*a*, fig. 102) will not be smooth and continuous, as some writers seem to think. If we superpose atmospheric absorption, the emission curve of quartz (curve *c*, fig. 101) will be somewhat as shown in curve *b*, fig. 102. Transmission curve *c* (fig. 102) is

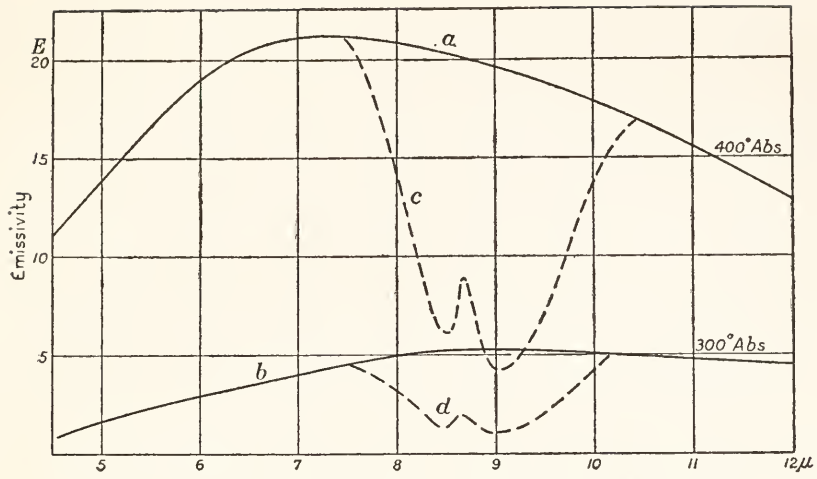

FIG. 101. — Emission of complete radiator (*a*) and (*b*); Emission of quartz (computed).

for a column of air 110 meters in length, containing 1.2 mm. precipitable water,[1] and is due to Langley (*loc. cit.*). A thick layer would shift the maximum at 8 μ toward 8.3 μ found in the moon's radiation curve. In fig. 103, curves *a*, *c*, and *d* show some of Langley's observed lunar radia-

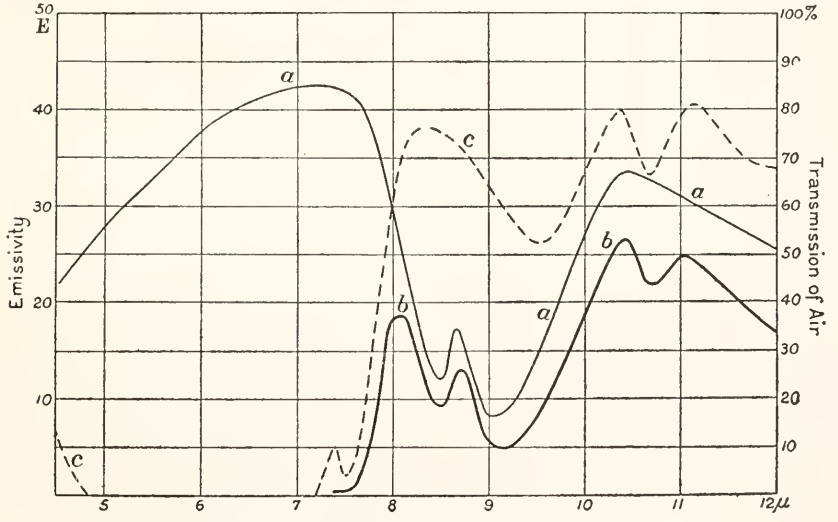

FIG. 102. — Emission of quartz (curves *a* and *b*); transmission of air (Langley).

tion curves, and as a whole there is a close parallelism between the theoretical curve *b*, from fig. 102, and the observed curves, at 10.7 μ, where we have to consider only atmospheric absorption. From 8 to 9 μ, however,

[1] Apparently water-vapor is more transparent than a film of the liquid, for a film of even one-tenth this thickness is opaque to heat rays beyond 5 μ.

we have to consider the combined effect of atmospheric absorption, of incomplete emission of the moon (emission minima from 8.5 to 9.8 μ), and of selectively reflected energy from the sun. The latter will, no doubt, vary the most in intensity. The computed emission curve is the most intense at 10.2 μ, while the observed is the most intense at 8.3 μ (see fig. 103). This is to be expected if the observed energy curve is the composite of the selectively emitted energy of the moon, and the selectively reflected energy of the sun, which is selectively transmitted by the earth's atmosphere. The selectively reflected energy of the sun would to a certain extent fill up the minima in the lunar emission curve, thus making it higher at 8.3 μ than at 10.2 μ, and, as far as our present knowledge goes, would explain the observed curves *a*, *c*, *d*, fig. 103, which lack a minimum at 8.5 μ. As

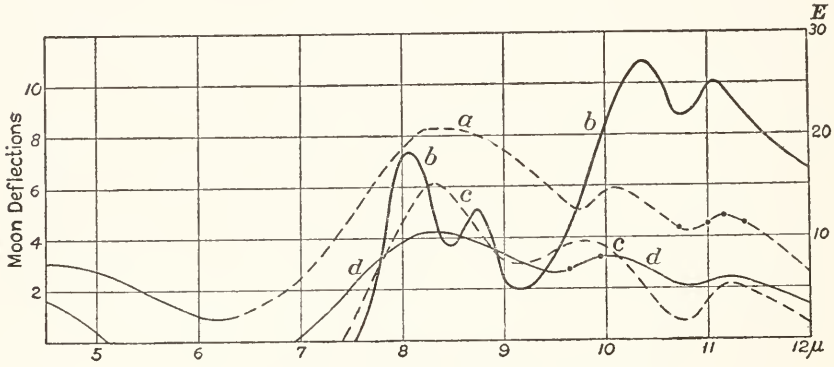

FIG. 103. — Emission of quartz (*b*); Emission from moon (Langley).

a whole, from whatever standpoint we view this matter we come to the same conclusion, viz, that in the region from 8 to 10 μ the energy emitted from the moon consists of its own proper radiation and of reflected energy from the sun.

To sum up, we know that Langley observed radiation from the moon in the region of 8 to 10 μ. He observed also direct radiation from the sun in this same region; but we do not know how much of this is superposed upon the direct radiation from the moon due to the latter being selectively reflecting in this region of the spectrum. As stated in Carnegie Publication No. 65, page 115, computations which require all sorts of assumptions will not settle the question. Bolometric comparison of the spectrum energy curves of the sun and of the moon made at high altitudes will be of greater service in clearing up the matter. Very's[1] suggestion of searching for a solar image in the lunar image, with a delicate heat-measuring instrument covered by a screen with a pin-hole aperture, also deserves a thorough trial. Exception has been taken to the writer's statement (*loc. cit.*) that, of the radiation observed by Langley in the lunar spectrum at

[1] Very: Astrophys. Jour., **24**, p. 353, 1906.

8 to 10 μ, we do not know how much is selectively reflected energy from the sun. But the writer maintains that just as soon as we admit the possibility of the moon being selectively reflecting in the region where it has its own proper radiation, then the use of glass[1] as an absorbing screen for testing the quality of that radiation is inadmissible, although it does serve as a rough test of the reflected energy at 0.5 to 3 μ. For this purpose it has been serviceable, and when we consider the great difficulties under which such work must be carried on, and the numerous corrections that must be introduced (which at all times may be larger than the one for selective reflection), the use of a glass screen is not objectionable.

Furthermore, we have noticed that the silicates reflect as a transparent medium in all regions of the spectrum considered, except from 8 to 10 μ, where it reflects like a metal. This means that the reflected energy in all these regions except 8 to 10 μ will consist of two parts, viz, that reflected from the outer surface and that due to internal reflection. From 8 to 10 μ there will be but little, if any, energy due to internal reflection. Hence, to use the reflected energy spectrum of the moon from 0.5 to 4 μ as a means of estimating the amount of reflected energy at 8 to 10 μ is not a fair test, and, as used (for want of better data) in the present paper, can only serve as an approximation. As in the case of emission spectra, it ought to be possible to analyze a substance by means of its reflection bands. The constitution of an isolated body like the moon, shining by reflected light, might thus be determined. This will probably never be possible since terrestrial atmospheric absorption will interfere with the observations, while a far greater sensitiveness in the radiometers will have to be attained than now is possible.

From whatever standpoint we view the matter, the conclusion is that the lunar surface must be diffusively, selectively reflecting, however small. Hence, in the stream of energy reflected in any direction from the lunar surface the density will be greatest for the wave-lengths of the bands of selective reflection. One would, therefore, expect to detect this difference in all directions, and not simply at the angle of reflection as suggested by Very (*loc. cit.*). It is difficult to apply a thorough test which will determine whether, and how much of, the energy from the moon is due to emission, and how much is due to reflection of energy from the sun. A rigid comparison of the energy curves of the sun and the moon in this region would be of great value. The polarization of the radiation from the moon might also be of use in deciding this point. Pfund[2] has shown that

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[1] Various observers have compared the total radiation from the moon to that part which is transmitted by glass. Glass being opaque beyond 4 μ was assumed to absorb the proper radiation from the moon, while the part transmitted by glass was considered to be reflected energy from the sun. Evidently if there is selectively reflected energy of the sun beyond 4 μ, then it will be superposed upon the direct radiation of the moon, and the use of a glass screen for testing the lunar radiation is inadmissible.

[2] Pfund: Astrophys. Jour., **24**, p. 19, 1906.

the bands of residual rays reflected from calcite are elliptically polarized. Pflüger[1] studied the polarized radiation from tourmaline heated to high temperature. Further than this, nothing is known concerning the polarization of the radiation emitted by substances like the silicates; hence this test might not be very decisive.

To subject the above conclusions to experiment in which the reflection of a rough surface is to be measured will be accompanied with difficulties because of the smallness of the surfaces that can be used.[2] In the case of the moon an image of the whole, or a greater part of the surface, may be projected upon the spectrometer slit. This means concentrating radiation which comes from a surface many miles in diameter, as compared with a surface which, when produced in the laboratory, amounts to only a few square centimeters.

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[1] Pflüger: Ann. der Phys., **7**, p. 800, 1902.

[2] Since writing this, Dr. A. Trowbridge, at the Washington meeting of the American Physical Society, April 24–25, 1908, described a series of experiments on the diffuse reflection of infra-red energy, in which he showed that powdered quartz has minima of diffuse reflection in the regions where there are absorption bands (*e. g.*, 2.95 μ), and reflection maxima at 8 to 9 μ, just as obtains for plane surfaces. This is an excellent illustration of the difference of what corresponds to body color and surface color in the visible spectrum (see Wood's Optics, p. 352). It also illustrates the question of diffuse selective reflection discussed on a previous page.

APPENDIX I.

THE EFFECT OF THE SURROUNDING MEDIUM UPON THE EMISSIVITY OF A SUBSTANCE.

In most of the problems in radiation from substances the surrounding medium is air, and no account is taken of the refractive index, which is taken as unity. In a remarkable research on "The Formation of River Ice with Special Reference to Anchor Ice and Frazil," by H. C. Barnes, it is shown that the surrounding medium plays an important part in the rate of cooling of the earth's crust.

In Canada, as well as other localities having high latitudes, three kinds of ice are observed, viz, sheet or surface ice, frazil ice, and anchor ice.

Surface ice is found only in still water, and is caused by the loss of heat to the cooler atmosphere, by radiation and conduction from its surface. Thickening of the ice-sheet takes place downwards by conduction of heat through the ice to the air.

Frazil ice is the French-Canadian term for fine spicular ice, from the French for forge-cinders, which it is supposed to resemble. It is found in all rivers or streams flowing too swiftly for the formation of surface ice. A dull, stormy day, with the wind blowing against the current, is productive of the greatest amount of frazil ice, which, like anchor ice, has a tendency to sink upon the slightest provocation, and to follow submerged channels until it reaches a quiet bay. Here it rises to the under side of the surface ice, to which it freezes, forming a spongy growth, attaining great thickness; in some cases the author observed a depth of 80 feet of frazil ice.

Anchor ice, as the name implies, is found attached or anchored to the bottom of a river or stream, and often attains a thickness of 5 to 6 feet. It is also called ground-ice, bottom-ice, and ground-gru. In a shallow, smooth-flowing river we are more likely to have anchor ice formed in excess, whereas in a deep and turbulent stream we are likely to have more frazil. In a river 30 to 40 feet deep anchor ice is almost unknown, although large quantities of frazil are met with.

Barnes remarks that —

> The various facts of common observation in connection with anchor ice points to radiation as the primal cause. Thus it is found that a bridge or cover prevents the formation of anchor ice underneath. Such a cover would act as a check to radiation, and reflect the heat-waves back again to the bottom. Anchor ice rarely forms under a layer of surface ice covered with snow. It forms on dark rocks more readily than on light ones, which is in accord with

what is known in regard to the more copious radiation of heat from dark surfaces. Anchor ice never forms under a cloudy sky either by day or by night, no matter how severe the weather, but it forms very rapidly under a clear sky at night. Anchor ice is readily melted off under a bright sun. It seems highly probable, then, that radiation of heat supplies the necessary cooling to the bottom of a river to form the first layers of ice, after which the growth or building up of the ice is aided by the entangling and freezing of frazil crystals, which are always present in the water.

The author found that during rapid ice formation the water becomes slightly undercooled to the order of a few thousandths of a degree, and that the ice which is found is in a very adhesive state. On the cessation of cold weather the temperature of the water rises slightly above the freezing-point and the ice gradually melts. Anchor ice rises from the bottom in mild weather and also in extreme cold weather under the influence of a bright sun, when it is dangerous to small boats. It is also known to lift and transport large boulders. On the other hand, a bright sun prevents the water from becoming undercooled and the formation of frazil ice. The author's conclusion that anchor ice is formed by radiation rather than by conduction is practically the same as that of Farquharson in 1841.

At the request of the editor of the Monthly Weather Review, the writer[1] has inquired into the aforesaid conclusions, which at first seemed untenable. After considering various experimental data, it appears to the present writer that the explanation of Farquharson and of Barnes accounts for the observed phenomena better than any of the other theories propounded. Thus the loosening of the anchor ice under a bright sun is simple enough from the fact that water is transparent to heat-waves up to 1 μ. The thickness of the layer of ice that must be melted in order to overcome the adhesion to the rock surface must be of molecular dimensions. In addition to this, there is the tension on the rock surface due to the buoyancy of the ice, which also tends to melt the ice. The explanation of the formation of anchor ice is more difficult, and the author's statement that "it is not to be supposed, because a substance like water has been found to be highly opaque to the radiation from hot bodies, that it will be the same for cold body radiation" is a little startling, and not very clear, for the transmissivity of any region of the spectrum is independent of the temperature of the source. However, if total radiation is meant, then such an interpretation is possible. In "Investigations of Infra-red Spectra" (Carnegie Publication No. 35), several examples, *e.g.*, methyl iodide, are given, illustrating the latter case. There is no evidence, however, for saying that "it is probable that water possesses an absorption band for shorter heat-waves, but may become perfectly transparent for the longer heat-waves." It is known that water is exceedingly opaque to heat rays from 4 to 8 μ followed by a more transparent region from 8 to 20 μ (this

[1] The Monthly Weather Review, p. 225, May, 1907.

was found by Rubens and Aschkinass[1] for water-vapor, which behaves like the liquid in its properties for absorbing heat-rays), beyond which there is great opacity. In fig. 104 is given the transmission curve of a column of 75 cm. of water-vapor (due to Rubens and Aschkinass, *loc. cit.*), from which it will be noticed that there is a quite transparent region from 8 to 15 μ. They found that the heat waves at 51 μ were entirely absorbed, while at 80 μ theory (see Drude, Optik, p. 359) predicts a band of metallic reflection. Moreover, water differs from most other substances in that its great opacity is due to numerous *small* absorption bands. Consequently its absorption coefficient is smaller than that of a substance like quartz which has bands of metallic reflection at 8.5, 9.02, and 20.75 μ. Hence, there is no objection to saying that "the whole question of the formation

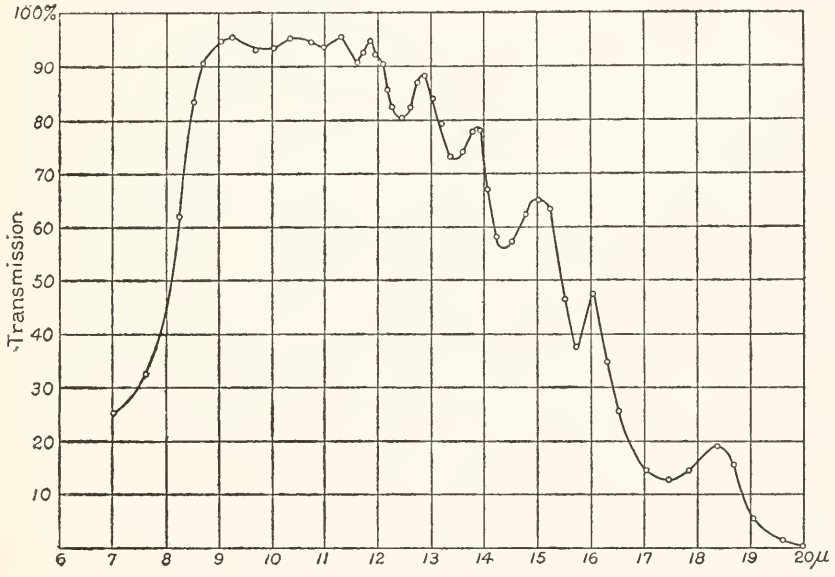

FIG. 104. — Transmission of water vapor.

of anchor ice depends upon admitting that the long heat-waves can penetrate freely through the water," for the maximum radiation of a body at a temperature of 0° C. lies in the region of the spectrum extending from wave-lengths 8 to 20 μ, and it is here that water has its greatest transparency for long heat-waves.

It is difficult to conceive of a more complex form of radiation than the one here involved. According to Provost's theory of exchanges, when two bodies are at different temperatures the hotter receives energy from, and imparts energy to, the colder by radiation, and vice versa. In the case of the river, when the sky is clear, the water is radiating into space which is

[1] Rubens & Aschkinass: Ann. der Phys. (3), **64**, p. 584, 1898; also Ann. der Phys., **65**, p. 251, 1898.

probably at absolute zero of temperature. The river-bed is radiating energy into the water, and probably through it into space. Leaving out of consideration the special nature of the emissivity of the two bodies (water and river-bed), it has been established (see Drude's Optics, p. 462) that the radiation from a "non-black body" is approximately proportional to the square of the refractive index of the surrounding medium, which is transparent, so that, from this standpoint, the emissivity of the river-bed into the water would be greater than that of the water into the air. Of course, if water were perfectly transparent, its emissivity would be *nil*, and the problem would be less complex. Little is known concerning the special nature of these two bodies, but from the fact that the anchor ice separates so easily from the river-bed under a bright sun, it is evident that the absorption coefficient of rock material is greater than that of water, and hence, that its emissivity must also be greater. Hence, more energy will be radiated from the river-bottom than from the water, into space, the river-bottom will become the cooler, and finally a film of ice is formed on it. During cloudy weather the temperature of the water-vapor in the air is equal to or higher than that of the water and the river-bottom. There is then an equality in the radiation, or an excess is being emitted from the clouds to the earth. A certain amount will also be returned from the clouds by reflection. Hence, the excess of radiation is toward the earth, and since the temperature of the clouds is above the freezing-point no anchor ice is formed.

To sum up, from this elaboration of the author's explanation, just quoted, of the formation of anchor ice, it will be seen that it is not only possible, but also highly probable that the cause is to be attributed to the greater emissivity of the substances forming the bed of the river, and to the greater transparency of water to heat-waves than is generally supposed to obtain for that substance. It is difficult to conceive that such a condition can exist, but the magnitude of the heat transfer, required to bring about this ice formation, must be exceedingly small, and the explanation given accounts for all of the facts observed.

On a previous page the conclusion was reached that the energy received from the moon will be the composite of the selectively reflected energy of the sun and of the selectively emitted energy of the moon, which is selectively transmitted by the earth's atmosphere. In the same manner the earth would emit selectively in the region of 8 to 10 μ and less than a complete radiator at the same temperature. It is, therefore, hotter than a complete radiator which emits the same amount of energy. All these questions are of extreme importance to the meteorologist who is concerned with the cooling of the earth. It may be added, however, in conclusion that the loss of radiation from the earth under the above conditions must be exceedingly small. In the same manner the suppression and conservation of energy in the region of 8 to 10 μ must be very small, so that it is a

matter of speculation whether the earth would be at a much lower temperature if its surface were composed of material not having bands of selective emission.

Rubens and Aschkinass (*loc. cit.*) found that after four reflections from fluorite surfaces the deflection due to solar energy is reduced to zero, showing that the opacity of the combined solar and terrestrial envelope is practically total for wave-lengths 24 to 32 μ. In a recent communication on the absence of very long waves from the sun's spectrum, Nichols[1] found that the atmospheric transmission for wave-lengths $\lambda = 51\ \mu$ can not be greater than 3 per cent. This, however, does not indicate that the sun is lacking in radiation of wave-lengths $\lambda = 51\ \mu$, as the title of the paper appears to imply, but that, whatever the intensity of the radiation emitted at 51 μ, it is almost entirely absorbed by the earth's atmosphere.

[1] E. F. Nichols: Astrophys. Jour., **26**, p. 46, 1907.

APPENDIX II.

INSTRUMENTS AND METHODS USED IN RADIOMETRY.

There are few fields of experimental investigation so beset with difficulties as the quantitative measurement of radiant energy. This is due to the fact that the radiation to be measured is generally from a surface of which it is practically impossible to determine the temperature. The measurement of radiant energy usually involves its transformation into some other form, and the receiver used for this purpose is subject to losses by heat conduction within, and by reflection, radiation, and convection losses from its surface.

As a result of inquiry into the development of the various instruments and methods used in measuring radiant energy, viz, the radiometer, the thermopile, the radiomicrometer, and the bolometer with its auxiliary galvanometer, the writer has accumulated extensive data, part of which is included here, with the hope that it may be useful to others interested in the subject.

Various instruments have been devised, the sensibility, or the possible chances for improvement, of which can be rated without further investigation. That in many cases the sensitiveness has been overestimated, will be noticed in the present paper. However, four instruments, viz, the radiomicrometer, the thermopile, the bolometer, and the radiometer, have been used extensively in radiation work, and in each case the inventor has found qualities which seemed to him to render his instrument superior to other types. But, to the writer's knowledge in no instance have all four instruments been studied by any one person; and, perhaps, it should not be expected. Each instrument requires a special mode of handling, and has peculiarities which can be learned and controlled only after prolonged use. This is particularly true of the radiometer and of the bolometer with its auxiliary galvanometer.

Having already had considerable experience with radiometers, one of which was the most sensitive yet constructed, the writer has, in this examination, devoted most of his attention to the bolometer. The investigation originated for the most part from the question whether the radiometer was selective in its action, in the region of the short wave-lengths. In previous work it was found[1] that the radiometer gave small deflections in the violet spectrum of the arc where Snow,[2] using a bolometer, found large deflections.

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[1] See Investigations of Infra-red Spectra. Part II. Infra-red emission spectra. (Carnegie Publication No. 35.)

[2] Snow: Physical Review, 1, p. 32, 1893.

In the course of the discussion it will be noticed, as was previously shown in a general way, that each instrument has some quality which makes it useful for a certain kind of work. For measuring very narrow emission lines and determining dispersion curves the bolometer is no doubt the best adapted. For measurements requiring a larger receiving surface, the linear thermopile is the more sensitive and the more precise. It has the further advantage that there is no permanent current. On the contrary, the bolometer has a current which heats the bolometer strip above the temperature of the surrounding air. This causes air currents which make the zero unstable. This is not true of the thermopile. Less is known concerning the radiometer, which rivals the bolometer and the thermopile in sensitiveness. Furthermore, the radiometer is not subject to magnetic perturbations. Its window limits its usefulness to the region of the spectrum up to 20 μ. The fact that it is not portable is a very minor objection.

I. THE MICRORADIOMETER.

Since we are concerned with radiation meters of the greatest sensitiveness, the ingenious device of Weber,[1] called the microradiometer, deserves passing notice. The instrument is not unlike a combination of a differential air thermometer and Wheatstone bridge. Two arms of the bridge consist of a thin glass tube containing a bit of mercury at the center with a solution of zinc sulphate at the ends, into which dip platinum electrodes. The ends of the bulbs are covered with rock-salt windows. If radiant energy is allowed to enter one of these bulbs, the air expands and pushes the liquids toward the opposite bulb. This will change the relative lengths of the column of mercury and of the solution between the platinum terminals, which means a change in resistance in the bridge arm, and a consequent deflection of the galvanometer. The instrument was stated to be sensitive to a temperature change of 0.00001°, and while it is not adapted to spectrum radiation measurements, it might be used in total radiation work where an elaborate installation is not convenient. By making the receiving bulb of opaque non-conductive material and by covering the inside with lampblack, or platinum black, this would be as complete an absorber ("black-body") as the thermopile or bolometer. Its efficiency would, of course, depend upon the gas inclosed.

II. THE RADIOMICROMETER.

The radiomicrometer is essentially a moving coil galvanometer, of a single loop of wire, with a thermo-junction at one end. This instrument was invented independently by d'Arsonval[2] and by Boys.[3] The former

[1] Weber: Archiv. Sci. Phys. et Mat. (3), **18**, p. 347, 1887.
[2] d'Arsonval: Soc. Franç. de Phys., pp. 30 and 77, 1886.
[3] Boys: Proc. Roy. Soc., **42**, p. 189, 1887.

used a loop, one part of which was silver and the other was of palladium; the latter used a junction of bismuth and antimony, which was soldered to a loop of copper wire.

The sensibility of the Boys instrument was given as $\frac{1}{10\,000\,000}$ to $\frac{1}{94\,000\,000}$ of 1 degree. From subsequent work with other radiation meters in which this high degree of sensitiveness has never been attained, it would appear that the sensibility of the radiomicrometer was overestimated. It certainly has never attained the sensibility of the radiometer, one example of which, used by Nichols (*loc. cit.*, Table V), was twelve times as sensitive as the radiomicrometer of Boys. The latter gave a deflection of a little less than 1 cm. per square millimeter of exposed vane for a candle and scale, each at a distance of 1 meter. Paschen[1] attempted to improve the radiomicrometer, but out of about fifty junctions only three were useful, and these were only three times as sensitive as that of Boys, while the period was about 40 seconds. The long period is not always detrimental, however, for the radiomicrometer is not subject to magnetic disturbances and is a very useful instrument for work not requiring the highest attainable sensitiveness.

The writer has indicated further improvements in the instrument (see Carnegie Publication No. 65) and places it in a vacuum, which increases the sensibility by at least 70 per cent. The instrument was about six times as sensitive as that of Boys for a full period of 25 seconds. Para- and dia-magnetism limited the sensitiveness to this value. The work with this instrument brought out the fact that one is inclined to use too strong field-magnets, and that further progress can be made by using weak magnets, or narrow strong magnet, situated as far as possible above the thermo-junction, so as to avoid the effects of para- or dia-magnetism. The combination of the radiomicrometer and the radiometer is feasible, although the writer found its usefulness as limited as that of the radiomicrometer. When wires can be obtained more free from magnetic material it will possible to construct a more sensitive instrument. It is doubtful, however, whether it will ever surpass the bolometer used with a galvanometer of the highest sensibility. With the radiomicrometer, Lewis[2] was able to investigate infra-red emission spectra of the alkali metals, which are weak in energy. Wilson[3] and Julius[4] have used the radiomicrometer for total and spectral radiation work, and have found the instrument highly satisfactory. The slow period and lack of portability, mentioned by some writers, is certainly not to be weighed against its indifference to magnetic perturbations and constancy of the zero reading. Even a slow period is less objectionable than a quick period instrument

[1] Paschen, Ann. der Phys. (3), **48**, p. 272, 1893.

[2] Lewis: Astrophys. J., **2**, p. 1, 1895.

[3] Wilson: Proc. Roy. Soc., **55**, 1894; **58**, 1895; **60**, p. 337, 1896.

[4] Julius: Handlingen **5**, de Nederlandisch Natuur- en Geneeskundig Congres, 1895.

with which just as much time is lost by repeating observations which may be affected by the lack of constancy of the zero. The instrument is self-contained, and where the greatest sensitiveness is not required, it deserves a wider application.

TABLE IV. — SENSITIVENESS OF RADIOMICROMETERS AND RUBENS THERMOPILE.

Observer.	Full period.	Area of vane.	Deflections in cm/mm² candle and scale at 1 m.
Radiomicrometer:	*sec.*	*mm²*	*cm.*
Boys (Phil. Trans., **180 A**, p. 159, 1889)	10	4	0.9
Paschen (Wied. Ann., **48**, p. 275, 1893)	40	.....	3
Lewis (Astrophys. Jour., **2**, p. 1, 1895)	20	1.4	1.3 (?)
Coblentz (Bulletin Bureau of Standards, **2**, p. 479, 1906).....	40	3	3.6
Thermopile:	25	3	6 (in vacuo)
Rubens (Wied. Ann., **45**, p. 244, 1898)	14	16 (?)	16(250 cm. total deflection) 1 mm = $1.1° \times 10^{-6}$ C.

In table IV are given the various radiomicrometers thus far described and their sensitiveness, which is expressed in centimeter deflections per millimeter of exposed vane, for a candle and scale each at a distance of 1 meter.

III. THE THERMOPILE.

From a historical point of view the thermopile has been in use from the very beginning of radiant energy measurements, and in the hands of Tyndall and other pioneers in this domain rendered excellent service in spite of its great heat capacity. For spectro-radiometric work, however, only the linear thermopile of Rubens[1] is well adapted. This thermopile consists of 20 junctions of iron and constantan wires about 0.1 mm. to 0.15 mm. thick (resist 3.5 ohms), and when used with a galvanometer, having a figure of merit of $i = 1.4 \times 10^{-10}$ amp. (period = 14 sec.), a deflection of one scale division indicated a temperature change of $1.1° \times 10^{-6}$. A candle at 5 m. gave a deflection of about 10 cm. or 250 cm. at 1 m. The area of the exposed face is about 0.8×20 mm. The deflections were as rapid as a bolometer, and its stationary temperature was reached in less time than the single swing of the galvanometer needle. In other words, its heat capacity was so small that it gave an accurate register of the energy falling upon it. In another experiment, using a galvanometer sensitiveness of $i = 5 \times 10^{-10}$ ampere, and the scale at 1 m., 1 mm. deflection = $2.2° \times 10^{-6}$ C. The sensitiveness is the same as that of the best bolometers yet constructed, while its simplicity commends itself even in spectrum radiation work.

The general experience in this country, however, has been that the commercial instrument does not fulfill all the excellent qualities claimed for the one originally described. The wires are heavier than in the original specifications, which makes the instrument sluggish.

[1] Rubens: Zs. für Instrumentenkunde, **18**, p. 65; 1898.

The problem in thermopile construction is to have it of low resistance (equal to that of the galvanometer), of low heat capacity and heat conductivity, and of high thermoelectric power. The latter requirement is fulfilled by using iron and constantan. The heat capacity can be reduced by using finer wire, say 0.06 to 0.1 mm. diameter, and by making the unexposed junctions smaller than the ones to be exposed. The latter are soldered with quite large beads of silver, which are then flattened to present a large surface. The unexposed junctions do not need this, and the small bead formed by the fusion of the two wires (with a bit of silver solder if necessary) can be hammered thin, in order to have it radiate rapidly. By using finer wires the resistance will be increased if the dimensions of the Rubens pile be retained. In the commercial instrument, at least one-third of the wire is between the unexposed junctions and the binding-posts. The greater part of this wire may be eliminated by making the supporting frame narrower, while still retaining the original distance between the exposed and the unexposed junctions. The elimination of this superfluous wire will reduce the resistance by about one-third.

Comparison of Old and New Form of Thermopile.

In order to test these conclusions in regard to the use of finer wire, a new iron-constantan pile of 20 junctions, made of wire 0.08 mm. diameter, was ordered from the makers of the original instrument. Although the specifications were not completely fulfilled (the frame was nearly the same size as the original, which increased the resistance to 9 ohms), the sensitiveness was 1.4 times that of the old type which has resistance of 4.8 ohms (wire about 0.15 mm.). By means of suitable switches the two thermopiles were connected to the same galvanometer, having a full period of 12 seconds ($i = 2 \times 10^{-10}$ amp.) and exposed to the radiation from a Nernst heater. For all deflections, as large as 35 cm., the new thermopile showed no drift greater than 2 mm., which may be attributed to the galvanometer. On the other hand, the zero of the old thermopile would drift 0.5 cm. in a 10 cm. deflection to 2.2 cm. in a 27 cm. deflection and would require 16 to 20 seconds for the deflection to return to its original zero.

The two instruments were then tested in a vacuum. The sensitiveness of the old instrument was increased only 15 per cent, while no change in sensitiveness could be detected in the new one, although two distinct tests were made on different days, the pressure having been reduced to 0.01 mm.

The thermopiles are mounted on ivory frames and are covered with a sheet of copper, one side having a slit, the other a funnel-shaped opening (1 by 15 mm.) in it. The slit was covered and the radiation passed through the funnel. The whole was suspended from a rubber cork in a wide-mouthed bottle, which was exhausted with a mercury or a Geryk pump. The source of energy was an incandescent lamp. With 200 ohms in series with the galvanometer the deflections were about 10 cm. The fact

that the sensitiveness of these thermopiles did not increase appreciably in a vacuum is rather remarkable. Brandes (Phys. Zeit., 6, p. 503) found that a single junction of 0.02 mm. wire became 18 times more sensitive in a vacuum. Lebedew (Ann. der Phys., 9, p. 209) found that a 0.025 mm. iron-constantan junction when black was 7 times, and when bright 25 times more sensitive at a pressure of 0.01 mm. than for atmospheric pressure.

The Peltier Effect.

The result of the Peltier effect is to lower the temperature of the exposed junction. Consequently, the thermopile does not give an accurate record of the energy received. The actual error introduced has never been determined. Since there is a possibility of using the thermopile for quantitative work in place of the bolometer, it is desirable to learn the degree of accuracy of this instrument.

The rate of generation of heat by the Peltier effect is proportional to the current, while the generation of heat on account of resistance is proportional to the square of the current. Jahn[1] has shown that the heat generated by the Peltier effect, determined experimentally, agrees, within experimental error, with the value computed from the observed thermoelectric power. The value for iron-constantan has never been determined experimentally[2] but from the work of Jahn it is permissible to compute the heat generated in the thermopile by using the known thermoelectric power which is about 50×10^{-6} volts.

Using a galvanometer of 5 ohms resistance and having a figure of merit of $i=3\times10^{-10}$ ampere per millimeter for a scale at 1 m., and an iron-constantan thermopile of 20 junctions, wire 0.08 mm. and 5 ohms resistance, 1 mm. $=2^{\circ}\times10^{-6}$ C. The Peltier effect in calories is computed from the formula

$$P=\frac{Tit}{J}\cdot\frac{dE}{dt}$$

where $T=274$; $i=3\times10^{-11}$ c.g.s.; $t=5$ sec.; $J=4.2\times10^{-7}$ and $dE/dt=50\times10^{-2}$ c.g.s. units;

$$P=\pm5\times10^{-12}\text{ gr. cal.}$$

The total weight of the junctions is about 0.01 gr. and the specific heat is about 0.1 gram calorie. Hence the temperature change of the exposed junctions is:

$$\Delta t=\frac{5\times10^{-12}}{0.1\times0.01}=5^{\circ}\times10^{-9}\text{ (for 1 mm. deflection)}$$

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[1] Jahn: Wied. Ann., **34**, p. 755, 1898.

[2] Since writing this, it has been found that Lecher (Ber. Akad. Wiss. Wien, **115**, p. 1505, 1906; Sci. Abstracts, 1083, 1907) has recently determined this constant to be 12.24 gr. cal. per amp. hr., while the value previously computed was 10.5 gr. cal. per amp. hr.

and since the temperature of the unexposed junctions is changed an equal amount in the opposite direction the total $\Delta t = 1° \times 10^{-8}$. But a deflection of 1 mm. $= 2° \times 10^{-6}$ C., hence the error is 1 part in 200 under the best theoretical conditions. In practice the temperature sensitiveness will not be so great; it will be shown presently to be of the order $5° \times 10^{-6}$, whence the Peltier effect would cause an error of 1 part in 500, or 1 mm. in 50 cm., which is as close as one can read such large deflections.

Since the Joule heat depends upon the square of the current it is negligible. Further consideration of the thermopile as an instrument for quantitative measurements will be found below in connection with the bolometer.

It will be noticed presently that prior to his construction of the iron-constantan thermopile, Rubens had used several very sensitive bolometers, all of which were displaced by the thermopile. For exploring spectra with very narrow lines, the linear bolometer is probably better adapted than the pile which, however, may be covered with a diaphragm, having a narrow slit. For extreme sensitiveness it equals the bolometer, and it is a noteworthy fact that all the investigations in the extreme infra-red and ultra-violet parts of the spectrum, where the energy is weak, have been accomplished by means of the thermopile. Unless one can build up an elaborate permanent bolometric apparatus in a room not exposed to direct sunlight, the thermopile will give the more reliable readings, as far as the constancy of the zero is concerned. Whether or not the thermopile will give a true reading of the energy falling upon it will depend upon the manner in which it is employed. It requires no particular skill to manipulate, and is easier to protect against temperature changes than is a bolometer with its storage battery. The "drift" in bolometers to be noticed presently was found in the old thermopile when used with a very delicate galvanometer. This was not due to unequal increments of resistance as in the bolometer, but to thermoelectric effects at the binding screws, to the connecting wires moving in the earth's magnetic field, and principally to the large heat capacity of the junctions. Most of these disturbances, however, are small and easily avoided in the Rubens type of thermopile. Since the bolometer strips and the balancing coils are of dissimilar material, it is also as subject to thermoelectric disturbances.

IV. THE RADIOMETER.

The manner in which an interesting scientific toy can be made to serve a useful purpose is well exemplified in the radiometer of Crookes,[1] discovered about 1875. By fastening bits of pith (the one black, the other white) at the ends of a long straw, which was suspended by means of a silk fiber in a long glass tube, he was able to make measurements of

[1] Crookes: Phil. Trans. (II), 166, p. 325 1876.

radiant energy, even at that early date. Pringsheim[1] simplified the instrument somewhat, suspended the vanes bifilarly with silk thread, and used it to investigate the infra-red spectrum of the sun to about 1.5 μ, produced by means of a glass prism. From this, the first really useful radiometer was developed by Nichols.[2] The behavior of the radiometer has been worked out theoretically by Maxwell[3] in his paper on "Stresses in Rarefied Gases arising from Inequalities of Temperature." Among other things he showed that for two parallel disks very near each other the central points will produce but little effect, because between the disks the temperature varies uniformly, and only near the edges will there be any stress arising from an inequality of temperature in the gas. It has been shown by others, especially by Crookes and by Nichols, that the sensitiveness of the radiometer is a function of the pressure of the residual gas, of the kind of gas surrounding the vanes, and of the distance of the exposed vanes from the window. The latter, on account of its absorption, of course limits the region of the spectrum which is to be investigated. If the vanes are not too close to the window, the deflections will be proportional to the energy falling upon one of them.

Comparison of Sensitiveness and Area of Vane.

For veins of finite dimensions, such as must be used in practical work, the writer has found that the deflections are proportional to the area of the exposed surface of the vane. This is perhaps to be expected, although there seemed to be some doubt. The curve of deflections and exposed area of vanes (area 10.5×1.3 mm. for constant pressure of 0.02 mm.) does not pass through the origin. One explanation may be that for infinitely narrow vanes the graph is not a straight line, but curves as it approaches the origin. Because of the impracticability of suspending vanes of different widths successively from the same fiber suspension, at the same distance from the window, using the same gas pressure for all vanes, it was necessary to use one wide vane, with a slit before it, and vary the opening of the slit. The source of energy (Nernst heater) was at a distance of 3 meters and, hence, the width of the projection of the slit upon the vane was practically the width of the slit, except for a very narrow slit when diffraction may decrease the energy incident upon the vane. This, however, would displace the graph still farther from the origin. The forces acting in a radiometer are so complex and so little understood that no further examination was made to ascertain the limits within which the above proportionality holds. The test was made to reduce the deflections to unit area between the above limits of exposed vane. It is of interest to note in this connection that in a bolometer the sensitiveness varies as the square root of the area of the bolometer strip.

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[1] Pringsheim, Ann. der Phys. (3), 18, p. 32, 1883.

[2] Nichols: Phys. Rev., 4, p. 297, 1897; Berl. Ber., p. 1183, 1896.

[3] Maxwell: Collected Papers, 2, p. 681; Phil. Trans., Part I, 1879.

In his earlier communications the writer held to the belief that the weight of the vanes and their size were the most important factors in determining the sensitiveness and period of a radiometer. However, so many factors enter into the problem that it is difficult to decide this point, and the following test may be of interest, showing that the sensitiveness is determined principally by the diameter of the quartz fiber suspension.

Comparison of Sensitiveness and Diameter of Fiber Suspension.

Using the same vanes (0.5×9 mm. area) the sensitiveness and period were found for a heavy and a light quartz fiber suspension. The main difficulty was to insure that the vanes were at the same distance from the window, and that the pressure was the same in the two cases. Hence these qualities are only approximate. In table V, it will be noticed that in changing from a heavy to a light fiber the sensitiveness is increased 4.5 times while the period was increased almost threefold. It further shows that for the same (light) fiber the sensitiveness was doubled (36 to 71 cm. per mm.) by changing the pressure and the distance from the window, which was of fluorite, and hence opaque beyond 10 μ. The sensitiveness of 71 cm. per square millimeter of exposed area is the highest on record. This, however, was not the maximum sensitiveness since the pressure was 0.02 mm., while radiometers have their maximum sensitiveness at a pressure of about 0.05 to 0.1 mm. At this pressure, however, heat conduction would cause annoyance.

The vanes of this suspension were of platinum foil 0.01 mm. thick, covered on one side electrolytically with platinum black, and then smoked over a candle. (It is best to cool the gases from the flame by placing a wire gauze or sheet of metal full of holes between the flame and the vanes when smoking them.) These vanes were suspended by means of one of the finest workable quartz fibers, and when within 3 mm. of the window either one of the vanes would always approach and adhere to it, even at atmospheric pressure. From tests with fluorite windows, which from internal strains might be piezoelectric, and with rock-salt windows, when bare, and also when covered with tinfoil, it was found that this effect is not due to electrification. Starting with the vanes parallel, and at a distance of about 5 mm. from the window, it was found that as this distance was decreased one of the vanes (generally the one to be exposed to radiation) would approach the window, and for a distance of about 3 mm. would turn until the plane of the vanes was at right angles to the window. The observations extended over several months, and all evidence indicates that this effect is due to gravitational attraction. As a result of this the deflection of such a vane would not be proportional to the energy received. The radiometer had no torsion-head to control the zero. However, for general work with very sensitive radiometers a torsion-head would be necessary, since the best pumps may leak, which will cause a slow "drift."

It will be shown presently that this is about five times the sensitiveness of Snow's bolometer, for which 1 mm. deflection (scale at 3 m.) indicated a temperature difference of $7.5° \times 10^{-6}$. In other words, this radiometer would detect $\frac{1}{1\,000\,000}$ degree rise in temperature. But the period of the radiometer was 6 times that of the bolometer, which is its weakest point in radiation work requiring a short period.

TABLE V. — SENSITIVENESS OF RADIOMETERS.

Pressure.	Full period.	Deflection per square mm.	Remarks.
mm.	*secs.*	*cm.*	
0.02	45	7.9	Vanes (area 0.5×9 mm., weight 5 mg.) 3 mm. from window.
.02	60	11.5	Vanes closer to window.
SAME VANES (0.5×9 mm.), FINER QUARTZ FIBER.			
mm.	*min.*	*cm.*	
0.02	2	36	Vanes 3 mm. from window candle at 3 m.
.03	2.5	71	Vanes nearer window. This is the greatest recorded sensitiveness. A deflection of 1 mm. on scale at 1 m. $= 3.8° \times 10^{-6}$.
.04	.....	63.5	
HEAVY VANES, AREA 1.3×10.5 mm., WEIGHT 10+mg.			
mm.	*secs.*	*cm.*	
0.02	40	5.5	Distance of vanes from window unknown.
.02	60 to 64	13.7	Vanes nearer window, hence longer period.
.026	36 to 40	8.5	Vanes farther from window than in preceding.
.035	25	3.3	Vanes still farther from window, which shortens period and decreases sensitiveness. For a pressure of about 0.05 mm. the sensitiveness would be much greater.

A comparison can also be made (table V) between light vanes (0.5×9 mm.) and heavy ones (1.3×10.5 mm.) at the same pressure but having different quartz-fiber suspensions. The results show that while the light weight vanes are more sensitive than the heavy ones (see table V), there seems to be no limit to the sensitiveness attainable in either case, provided one does not consider the period. The idea of not considering the period of vibration with sensitiveness seems reasonable, for by sensitiveness is meant the minutest quantity of radiation one can detect, assuming one is willing to wait for the deflection to reach a maximum. In table VI are compiled the most notable radiometers used in radiation work. The use of a candle as a standard of comparison is questionable, but since the sensitiveness of the various instruments varies by a factor from 2 to 20, it is sufficiently accurate for the present comparison. In this table it will be noticed that for the same period the various radiometers vary in sensi-

tiveness by as much as 50 per cent. Porter's radiometer was the most sensitive of the instruments having a period of 90 seconds. But he gained little, on the whole, for the vanes were so light that he could work only during the quiet hours at night. On the other hand, the writer,[1] after trying light vanes, adopted the heavy ones, and was thus able to work at all hours, even with a large air-compressor in operation, in an adjoining room.

TABLE VI.—SENSITIVENESS OF VARIOUS RADIOMETERS.

Observer.	Full period.	Area of vanes.	Deflections per square mm. area of exposed vane; candle and scale each at 1 m.
	min. *sec.*	*sq. mm.*	*cm.*
E. F. Nichols:	0 12	2×15	5 (?)
Phys. Rev., **4,** p. 297, 1897			
Astrophys. Jour., **13,** p. 101, 1901	0 11	3.1	12.5
Stewart:	1 20	30	4.9
Phys. Rev., **13.,** p. 257, 1901	5		17
Drew: (Phys. Rev., **17,** p. 321, 1903)	1 30	7	17.1
Porter (Astrophys. Jour., **22,** p. 229, 1905)	1 30	3.6	27.5
Coblentz	1 30	15 (10×1.5)	8 to 10
Abs. Spectra	50	12	10 to 12
Phys. Rev., **16, 20,** and **22.** (Vac. tube)	1 40	11 (11×1)	52
Another vane	2 30	4.5	71
(*Ibid.*)	1 10	4.5	35

SENSITIVENESS COMPARED WITH WAVE-LENGTH OF EXCITING SOURCE.

In his investigations of emission spectra of the alkali metals, using a bolometer, and a prism and lenses of quartz, Snow[2] found that the vapor of the carbon arc had the larger portion of its energy concentrated in one large band in the violet. The writer,[3] using a radiometer, a rock-salt prism, and a mirror spectrometer for investigating infra-red emission spectra, found that the radiometer gave but small if any deflections in the violet. The violet band is far enough from the reflection minimum of silver not to be weakened by it, hence it appeared that the radiometer might be selective in its behavior to radiant energy.

To test this point the following experiment was tried. The total radiation from an aluminum spark (with glass plate condenser) on a 10,000 volt transformer was measured with a very sensitive radiometer (period 65 to 70 seconds; sensitiveness 35 cm. per square millimeter) just described, and with a bolometer, to be described subsequently. The window of the radiometer was of white fluorite 2 mm. thick, hence transparent to the ultra-violet, but opaque beyond 10 μ. A large point of the energy of the aluminum spark lies in the ultra-violet. The maximum energy of the warm electrodes occurs at about 8 μ. The radiation from the spark

[1] "Investigations of Infra-red Spectra," Carnegie Publication No. 35, 1905.

[2] Snow: Phys. Rev., 1, pp. 28 and 221, 1893.

[3] Carnegie Publication No. 35, Part II, 1905.

passed through a quartz cell 8 mm. thick, containing distilled water which absorbed all of the infra-red energy. The observations consisted in obtaining the ratio of energy transmitted by a glass plate 8 mm. thick (which is opaque to rays shorter than 0.3 μ) to the total energy of the spark.

Unfortunately, at the high sensitiveness required for ultra-violet radiation the two instruments were not in perfect working order at the same time. During the first test the bolometer had a short period, 10 seconds, and caused trouble by the "drifting" of the zero with changes in the spark, while in the second test the radiometer was leaking slightly, which caused its zero to "drift." Then, too, the spark was by no means constant, but, as will be seen presently, the ratio above referred to is about the same for the radiometer and the bolometer, after correcting for the loss of 4 per cent by reflection at the fluorite window. The agreement is close enough to show that the radiometer is not selective in its action and hence is adapted to investigations in the ultra-violet.

In the first test the direct radiation from the aluminum spark (with condenser) was compared with the part transmitted by glass. There was some infra-red energy in this case which made the ratio lower than in the second experiment. The direct deflections with the radiometer were about 20 cm. The ratio of the deflection through a piece of plate glass to the direct deflection varied from 17 to 19.5 per cent (mean about 18 per cent), while with the bolometer the same ratio varied from 16 to 20 per cent, the mean being about 19 per cent. The bolometer followed the flunctuations of the spark, hence the greater variations. The spark was 75 cm. from the radiometer and 25 cm. from the bolometer.

In the second test the infra-red radiation was absorbed by a cell of water, with quartz windows. Plate glass was again used to absorb the ultra-violet. In this test, the ratio of the radiation transmitted by the glass to the total radiation was on an average about 65 per cent, while the same ratio for the bolometer was 67 per cent. Correcting for the loss by reflection at the window the ratio for the radiometer would be about 69 to 70 per cent.

The results show that the radiometer is not selective, *i.e.*, it is as efficient in the ultra-violet as in the bolometer.

THE RADIOMETER COMPARED WITH THE BOLOMETER.

In discussing the merits of the radiometer, writers have generally emphasized the fact that the radiometer is not adapted for quantitative work since it cannot be calibrated. As a matter of fact, in reviewing the work done in radiation it was found that even with the bolometer there are only a few cases where the energy was obtained in absolute measure. Even in the study of the laws of radiation from a hollow enclosure or Kirchhoff radiator (so-called "black-body"), the direct galvanometer deflections were observed and reduced to a single standard of sensitive-

ness which was in arbitrary units. The same may be done with the radiometer. Its sensitiveness is easier to control, since it can be made to depend only upon the pressure of the residual gas — the constant of a galvanometer varies continually. It is not affected by magnetic effects, and a heavy vane is less affected by earth tremors than is a very light galvanometer suspension. It is sensitive to temperature changes, but less so than the bolometer, and it can be more easily shielded from temperature changes than can a bolometer with its galvanometer, battery, etc. The fact that it is not portable is not a serious drawback, since it is not usually necessary to move the instrument. It has two disadvantages, viz, its window, or preferably double window, is selective in its transmission, and its period is somewhat longer than that of a bolometer and galvanometer of equal sensitiveness. But the latter is nearly always drifting and to repeat one's readings it takes as long for an observation as it does with a radiometer.

Since the weight is of minor importance, tremors are avoided by having the suspension weigh about 8 to 10 mgs. When used with a good mercury-pump, it requires no attention after it is properly adjusted. A delicate galvanometer requires frequent adjustment and in connection with a bolometer the investigator's time is occupied principally with the care of the instrument (at least that has been the writer's experience), which should be a secondary matter. The two instruments are of the same order of sensitiveness, with the possibility of the radiometer being the more sensitive.

This is well illustrated in the test for their efficiency to ultra-violet radiation, where both instruments were at about their maximum working sensitiveness. The bolometer used was 0.22 by 10 mm. in area, resistance 2.8 ohms, and for a battery current of 0.04 amp. with a galvanometer sensitiveness of $i=1.5\times10^{-10}$ amp. (period 16 seconds) had a temperature sensitiveness of 9×10^{-6} per millimeter deflection, on a scale at 1 m. (see table VII). (A Nernst heater was also used in making the comparison.)

A candle at 1 m. gave a deflection of 45 cm. which, on the assumption that the sensitiveness is proportional to the square root of the area of bolometer strip, is 30 cm. per square millimeter. For the radiometer having a vane 0.5 by 9 mm. a candle gave a deflection equivalent to 159 cm. at 1 m. or, since the deflection is proportional to the area of the exposed vane, 35 cm. per square millimeter (table VI). In other words, the radiometer was 1.2 times as sensitive as the bolometer, or 1 mm. deflection corresponded to $7.5^{\circ}\times10^{-6}$ C. (For a full period of 2.5 minutes its sensitiveness was $3.8^{\circ}\times10^{-6}$ C.) Its period, however, was 4.5 times that of the bolometer. This estimation of sensitiveness is based on the assumption that the radiometer was as complete an absorber of energy as the bolometer. Judging from its period, its efficiency is much lower than

that of a bolometer, hence the radiometer must be sensitive to temperature changes less than the value just given.

The sensitiveness of bolometers thus far attained is about $\frac{1}{1\,000\,000}$ degree per millimeter deflection. Paschen claims a sensitiveness of $\frac{1}{10\,000\,000}$ degree by reading to 0.1 mm. But the conditions are rare when one can read to 0.1 mm., so that the estimate would seem too high. As will be seen presently, the working sensitiveness is of the order of $\frac{5}{1\,000\,000}$ degree, or generally considerably less.

V. THE BOLOMETER WITH ITS AUXILIARY GALVANOMETER.

We have now to consider one of the most useful radiation meters yet devised, viz, the bolometer which is simply a Wheatstone bridge, two arms of which are made of very thin blackened metal strips of high electrical resistance and high temperature coefficient, one or both of which are exposed to radiation. When thus exposed, their temperature changes, thus unbalancing the bridge, and the resulting deflection of the galvanometer gives a measure of the energy absorbed. The maximum sensitiveness of the bolometer is limited by the size of the strip and is proportional to the square root of the surface exposed to radiation. Any further gain in sensitiveness must be attained by increasing the sensitiveness of the galvanometer, which, for the moving magnet type, varies as the square of its (undamped) period. The sensitiveness is also proportional to the bolometer current, which is limited by the resistance of the bolometer strips.

It will be noticed presently that the working sensitiveness of the various galvanometers thus far used is of the order of 2×10^{-10} amp. per millimeter deflection, while the temperature sensitiveness varies from $5°\times10^{-5}$ to $5°\times10^{-6}$ for 1 millimeter deflection for a scale at 1 meter.

Historical.

The various bolometer-galvanometer apparatus will first be noticed, in so far as it relates to spectro-radiometric work.

The first great step in improving the moving magnet galvanometer is due to Kelvin who decreased the weight of the moving parts to a few milligrams, and introduced the astatic system of magnets. The main problem in bolometer construction is to use strips of a metal having a high resistance-temperature coefficient, a small specific heat, and low heat conductivity. These metals are nickel, platinum, tin, and iron, but for various reasons in mechanical construction, platinum is the most commonly used.

The manner in which this instrument has been developed to its present high sensitiveness is best illustrated by considering the various designs of different investigators, given in table VII.

TABLE VII.—BOLOMETER-GALVANOMETER SENSITIVENESS.

Observer.	Galvanometer.			Bolometer.		
	Resistance.	Full period.	Current sensitiveness for 1 mm. deflection.	Resistance.	Area.	Bolometer current.
	ohms.	*sec.*		*ohms.*	*sq. mm.*	*amp.*
Langley (Annals Astrohpys. Obs.)	.....	.....	$1 \text{ to } 5 \times 10^{-10}$	4	0.05 to 0.02 $\times 12$	0.03
Abbot (Astrophys. J., **18**, p. 1; 1903)	1.6	20	5×10^{-11}	.....	.....	.....
Ångström: Wied. Ann., **26**, p. 253; 1885.....	.....	.....	.....	.....	.....	.....
Wied. Ann. **36**, p. 715; 1889	.....	.....	.....	.....	0.1×12	.....
Wied. Ann., **48**, p. 497; 1893	8	16	5.7×10^{-9}	5	.....	.....
Julius (Licht und Wärmestrahlung, p. 31; 1890)	2.7	.....	4×10^{-9}	3	0.3×14	0.133
Helmholtz (Verh. Phys. Gesellsch., Berlin, **7**, p. 71; 1888)....	.....	.....	8×10^{-9}	8.8	.....	.....
Lummer and Kurlbaum: Zs. für Instrumentenkunde, **12**, p. 81; 1892.....	.....	.....	1.5×10^{-9}	60	$12 \times 1 \times 32$	0.006
Wied. Ann., **46**, p. 204; 1892						
Rubens: Wied. Ann., **37**, p. 255; 1889	5	4 to 5	3.2×10^{-10}	5.2	$7 \times 0.3 \times 35$	0.2
Wied. Ann., **45**, p. 238; 1892	80	.....	3.2×10^{-10}	3	$3 \times 0.2 \times 10$	.....

TABLE VII. — BOLOMETER-GALVANOMETER SENSITIVENESS.

Temperature sensitiveness.			Candle test.				Remarks.
For 1 mm. deflection and period given in col. 3.	Ibid., for a scale at 1 m.	Ibid., for a scale at 1 m. and a full period of 15 secs.	Distance of candle.	Distance of galvanometer.	Observed deflection.	Equivalent deflection per mm^2 area for candle and scale at 1 m.	
°C.	°C.	°C.	*met.*	*met.*	*cm.*		
1×10^{-6}	.....	.....	....	....	....	.....	In practice for solar spectrum work a full period of 3 secs. and $i=2.2\times10^{-9}$ ampere is used. Balancing coils of platinoid. Bolometer is inclosed in water jacket.
.....	.....	.....	....	....	....	.....	In practice drifting is minimized by placing a short copper wire in series with one of the bolometer arms.
.....	.....	.....	....	....	....	.....	Surface bolometer; 23 strips of tin foil; blackened with $PtCl_2$ and soot. Balancing coils of copper wire in separate box. Sensitiveness 556×10^{-9} gr-cals/cm^2/sec.
.....	.....	.....	....	2	....	.....	Single Pt. strip 0.1×12 mm. in spectrobolometer.
9×10^{-5}	.....	.....	....	....	....	.....	2 arms of tin foil in form of grating. Sensitiveness also given as 127×10^{-9} gr- cals/cm^2 sec.
.....	.....	.....	....	....	....	.....	Bolometer strips of nickel 0.002 mm. thick. Balancing coils of platinum wire in oil in separate box. Found deflection proportional to current.
8×10^{-5}	.....	....	....	....	....	.....	Surface bolometer, 4 similar arms, so no compensating resistances needed; diagonally opposite arms exposed. Sensitiveness also given as 533×10^{-9} gr-cals/cm^2/sec.
3×10^{-4}	.....	.....	1	....	800	.....	Surface bolometer 4 similar arms of platinum foil 0.001 mm. thick; 2 diagonally opposite arms exposed to radiation surface consists of 12 strips of platinum, 1 mm. wide×32 mm. long, separated by 1.5 mm., back of which openings are 12 similar strips of the diagonally opposite arm. Bolometer currents as high as 0.04 ampere could be used.
2×10^{-4}	.....	.....	....	....	....	.....	Surface bolometer of tin foil 0.01 mm. thick; 7 strips in each arm.
5×10^{-6}	2.5×10^{-5}	4×10^{-5}	1	5	60	5	2 arms of 0.04 mm. iron wire hammered flat; 3 strips in each arm.

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TABLE VII—CONTINUED.

Observer.	Galvanometer.			Bolometer.		
	Resistance.	Full period.	Current sensitiveness for 1 mm. deflection.	Resistance.	Area.	Bolometer current.
	ohms.	*sec.*		*ohms.*	*sq. mm.*	*amp.*
Rubens: Wied. Ann., **45**, p. 238; 1892	80	.....	3.2×10^{-10}	80	0.09×12	.....
Rubens and Snow (Wied. Ann., **46**, p. 529; 1892)	150	20	1.8×10^{-11}	80	0.09×12	.....
Snow (Phys. Rev., **1**, p. 31; 1893)	140	20	1.5×10^{-11}	75	0.05× 7	0.025
Aschkinass (Wied. Ann., **55**, p. 401; 1895)	.....	20	6×10^{-11}	13	.....	0.04
Donath (Wied. Ann., **58**, p. 609; 1896)	.....	.....	6×10^{-12}	5	.....	.....
Paschen (Wied. Ann., **48**, p. 272; 1893)	*60	7	2.3×10^{-11}	.....	.....	0.01 to 0.02
	*60	15	3.3×10^{-12}	.....	.....	.....
	20	30	1.6×10^{-11}	12	3×0.5×15	0.03
	..	34	8.3×10^{-12}	8	0.25 ×7	.02
Coblentz	5.2	10	2.5×10^{-10}	.....	.....	.....
	5.2	16	1.5×10^{-10}	2.8	0.22×10	0.02
Rubens Thermopile	5	14	1.4×10^{-10}	3.5	0.8×20	.....
Coblentz Radiometer	.....	70 ..	.....	.....	0.5×9	.....
	.....	150 ..	.....	.....	0.5×9	.....

*Galvanometer; 4 coils 40 mm. external and 5 mm. internal diameter, 1,200 turns of graded wire in each coil; moving system, 13 magnets in each group, 1 to 1.5 mm. long, on both sides of glass staff, and 0.3 mm. apart; mirror 2 mm. diameter × 0.03 mm. thick. Total weight of system = 5 mg.

TABLE VII—CONTINUED.

Temperature sensitiveness.			Candle test.				Remarks.
For 1 mm. deflection and period given in col. 3.	Ibid., for a scale at 1 m.	Ibid., for a scale at 1 m. and a full period of 15 secs.	Distance of candle.	Distance of galvanometer.	Observed deflection.	Equivalent deflection per mm² area for candle and scale at 1 m.	
°C.	°C.	°C.	*met.*	*met.*	*cm.*		
8×10^{-6}	4×10^{-5}	.....	1	5	12	2.7	2 arms of 0.005 mm. platinum wire hammered flat. Deflections of galvanometer proportional to current through bolometer and rise in temperture of arms proportional to incident energy.
3×10^{-6}	.....	.....	....	....	40	.....	For Hefner candle at 1 m.
8×10^{-6}	2.4×10^{-5}	4×10^{-5}	1	3	15	8.3	2 bolometer arms of platinum 0.000936 mm. thick; balancing coils of German silver; 4-coil galvanometer, total of 7200 turns, wound with two sizes of wire. Magnet system of 12 magnets 3 to 4 mm. long; total weight of system 80 mg.
3×10^{-5}	1.2×10^{-4}	.....	....	4	....	.....	2 bolometer arms of 3 iron wires hammered flat.
.....	.....	.....	....	....	....	.....	2 arms of platinum 0.17 mm. wide×0.0074 mm. thick; balancing coils (of platinum) of elaborate design in separate box. Drifting was serious.
.....	.....	.....	....	....	....	.....	Bolometer arms of platinum 0.001 to 0.0005 mm. thick.
.....	.....	.....	....	3	....	.....	Compensation resistances of manganin wire, final adjustment on platinum wire with mercury contact.
1×10^{-6}	2.7×10^{-6}	11×10^{-6}	....	2.7	....	.....	
84×10^{-7}	2.1×10^{-5}	8×10^{-5}	....	2.5	....	.....	
.....	.....	.....	....	....	....	.....	Using an 8-magnet system and a full period of 20 secs. $i=8\times10^{-11}$ ampere, while a 6-magnet system had a sensibility of $i=2.5\times10^{-11}$ ampere for a full period of 36 seconds.
.....	9×10^{-6}	9×10^{-6}	1	1	45	30	
1.1×10^{-6}	.....	1×10^{-6}	5	(1?)	10	15	
.....	†7.5×10^{-6}	.....	2.3	1	30	35	
.....	†3.8×10^{-6}	.....	3	1	35.5	71	

†These values are obtained by comparing the deflections per unit area with the bolometer.

Comparison of Sensitiveness of Various Bolometer-Galvanometer Combinations.

The most important data on sensitive radiation meters, and particularly that relating to bolometers, is given in table VII. It will be noticed that the thermopile is as sensitive as the bolometer. The sensitiveness of the radiometer is obtained by comparing it with the bolometer. Although the radiometer is no doubt less efficient than the bolometer, it probably absorbs as much of the incident energy. Since the radiometer deflections were larger, per unit area, than the bolometer deflections, it is safe to assume that the radiometer was just as sensitive as, if not more so than, the bolometer. The long period is of course a serious objection in certain classes of work. In table VII it will be noticed that the high temperature sensitiveness of the various instruments has been attained by the use of a highly sensitive, long period, galvanometer, by using a large bolometer current and by placing the scale at a great distance from the galvanometer. Assuming that the sensitiveness is proportional to the square of the period (undamped) for a scale at 1 m. and a bolometer current of 0.04 ampere, it will be noticed from column 10, table VII, that the temperature sensitiveness of the various instruments falls in two groups. To the first group belong the earlier instruments of Rubens, of Snow, and of Paschen, with a sensitiveness of about $5^{\circ}\times 10^{-5}$ per millimeter deflection. To the second group belongs a more sensitive combination of Paschen's, and the writer's instrument, in which 1 mm. deflection corresponds to a rise in temperature of $11^{\circ}\times 10^{-6}$ and $9^{\circ}\times 10^{-6}$ C., respectively. In other words, the instruments of the latter group have the same sensitiveness, and any increase in the same is to be attained by increasing the scale distance; the bolometer current of 0.04 amp. is about the limit for accuracy. The sensitiveness of the writer's instruments could have been further increased by lengthening the scale distance to 2.5 m., when the temperature sensitiveness would have been $3.6^{\circ}\times 10^{-6}$, and by doubling the galvanometer period, when the sensitiveness would have been $9^{\circ}\times 10^{-7}$ against Paschen's $1^{\circ}\times 10^{-6}$. Such a computation is, of course, illusory on account of damping in the galvanometer. On actual trial (but not for the magnet system quoted) for a full period of 30 seconds the sensitiveness of the galvanometer was $i=7\times 10^{-11}$ ampere.

Comparison of a Bolometer with a Thermopile.

The efficiency of the bolometer and the thermopile is reduced by losses due to reflection and radiation from the receiving surface, and by heat conduction to the unexposed parts. The loss of energy in the thermopile due to the Peltier effect has been considered in discussing that instrument. The loss of energy due to reflection is about 4 per cent (Kurlbaum, *loc. cit.*). Assuming the bolometer to be made of platinum 0.5×0.002 mm. cross-section, and the thermopile of 20 junctions of iron and constantan

wire 0.06 mm. diameter, it can be readily shown that the cross-section of the thermopile is about 56 times that of the bolometer, and from their heat conductivities, for the same temperature gradient, that the loss of heat by conduction in the thermopile is about 100 times that of the bolometer. But the temperature gradient at the ends of a bolometer strip carrying an electric current may be 50° to 100° C., so that the heat lost by conduction may be about the same for both instruments. Since the temperature of the bolometer is from 50° to 100° C. higher than the thermopile, the loss of heat per second due to radiation in the former is from 2 to 3 times that of the latter. But the mass of the thermopile is 5 times, while its specific heat is 3.3 times, that of the bolometer. Hence, to raise the temperature of thermopile and the bolometer to the same extent, 16 (5×3.3) times as many heat units must be supplied to the former. Since the loss by radiation is 3 times as great from the bolometer, it will require about 5 times as long for the thermopile to reach a steady temperature. In practice, however, on account of the blackening of the surface, the bolometer is not so quick in its action as here computed.

From these considerations, as well as the mechanical difficulties in constructing a thermopile of wire less than 0.05 mm. in diameter (and keeping the resistance low), it will be seen that the thermopile can not be made so quick in its action as the bolometer and hence is not so well adapted where a quick automatic registration of the galvanometer deflections is desired. But, as will be shown presently, since it is difficult to read large deflections accurately in less than a 4 to 5 second single swing of the galvanometer system, a thermopile of 0.06 to 0.08 mm. wire, which attains a steady temperature in this interval of time, is not objectionable, and, since it is less disturbed by air-currents (being at room temperature), it may be the more reliable instrument (see table IV). Neither instrument, however, compares with the radiometer in steadiness. The amount of work done on emission, absorption and reflection spectra, as well as the accuracy attained, in the infra-red to 15 μ, where the radiometer deflections were, again and again, only a few tenths of a millimeter would not have been possible with these instruments. In a recent examination of reflection spectra of minerals, using a thermopile, the accuracy attainable without repeating the readings several times was far from that of the radiometer, although the actual deflections were larger.

The present experimental comparison of the thermopile, of 0.08 mm. iron and constantan wire, and the platinum bolometer was undertaken in order to determine the accuracy attainable in measuring a constant source of radiant energy, and hence to learn the feasibility of substituting the thermopile for the troublesome bolometer. Within experimental error it has been established by Langley, by Rubens and by Julius that the bolometer (galvanometer) deflections are proportional to the current flowing through the bolometer, and also to the amount of energy falling upon the

bolometer strip. It remains, therefore, to determine whether the present bolometer behaves likewise, and also whether the same accuracy is attainable with the thermopile.

To this end a bolometer was constructed with the greatest care. It was annealed before adjusting the resistance of the strips, covered electrolytically with platinum black (after the method of Kurlbaum) and then smoked over wire gauze over a paraffin candle. The resistances of the bolometer strips were 1.782 and 1.797 ($\Delta = 0.015$) ohms, respectively. After blackening them they were 1.766 and 1.818 ($\Delta = 0.052$) ohms, respectively. The width of the bright strips was 0.5 mm., which increased to 0.56 mm. after blacking. The length was 11 mm. and thickness less than 0.002 mm. The bolometer current was 0.04 ampere and throughout the following experiments there was no difficulty due to air-currents, or drift. Magnetic disturbances were at a minimum, and, as a whole, conditions for accurate measurements were as perfect as one would expect.

The thermopile of 0.08 mm. wire (20 junctions covered with a slit 0.5 mm. wide) already described, showed a slight lag in registering the energy received. Although this was not marked, there was a tendency for the deflection to creep, instead of stopping abruptly as in the case of the bolometer. This was most marked in large deflections, and necessitated exposing the thermopile to radiation for a definite time (6 seconds) and taking the zero at the expiration of an equal interval of time. The results are given in table VIII. The last two values for the thermopile are vitiated by radiation from the rotating disk, to be noticed presently. The results show that there is no great difference in the two instruments. It was necessary, however, to note the time of exposure of the thermopile, which is not convenient for large deflections. The estimation of the relative merits of the bolometer and the thermopile is, therefore, a personal one, and from the experience gained it may be said that for measuring intense sources the bolometer is the more accurate (when working to 0.5 per cent) unless great precautions be taken in making the thermopile readings.

The theoretical temperature sensitiveness of the thermopile was considerably greater than that of the bolometer, as was found on subsequent computation. It may be added, therefore, that if the bolometer sensitiveness had been increased, by increasing the current through it, there would have been greater unsteadiness in the galvanometer readings.

Experiment with a Sectored Disk.

In comparing the relative merits of the bolometer and the thermopile, the simplest method appeared to be to reduce the intensity of the source by a known amount, by using a sectored disk, the angular openings of which are accurately known. It will be noticed that while the ratios of energy transmitted by the sectored disk were in close agreement in any series of measurements (see tables VIII and IX) the numerical values were

in all cases higher than the true ones. In other words, the disk transmitted too much energy, or the apparent opening was larger than the true one. It remained, therefore, to be shown whether this was due to diffraction (of the very long wave-lengths) or to lack of proportionality in the registering of the energy by the bolometer and the thermopile. The method of observation consisted in taking from 5 to 10 readings without the disk, then a similar number with the rotating disk interposed, followed by a number without the disk.

TABLE VIII.—COMPARISON OF BOLOMETER AND THERMOPILE.

Direct deflection (mean value).	Deflection with disk, 180°=49.9 (mean value).	Ratio.	Direct deflection (mean value).	Deflection with disk, 180°=49.9 (mean value).	Ratio.
Bolometer:			Thermopile:		
May 24, '07:			May 24, '07:		
12.22	6.14	*50.24	13.14	6.61	†50.26
12.16	6.11	*50.24	14.22	7.21	‡50.7
			14.30	7.24	‡50.6

* Nernst heater on 98 volts at 1 m. from bolometer. Galvanometer (full) period 8 seconds undamped; 50 ohms in series. Total deflection about 80 cm. Bolometer is perfectly steady and comes to rest abruptly. Readings vary from 0.1 to 0.7 per cent from mean of about 10 in each set. Temperature sensitiveness $= 6° \times 10^{-5}$.

† Conditions same as for bolometer. Thermopile deflection "creeps," and does not come to rest in same time as galvanometer (on open circuit or with bolometer), due to its larger heat capacity. Galvanometer single swing of 4 seconds increased to 6 seconds and is fully damped, due to lag of thermopile; 50 ohms in series with galvanometer. Temperature sensitiveness $= 2° \times 10^{-5}$.

‡ Source and disk nearer screen. Difficult to read deflection on account of "creeping," which amounts to 1 to 3 mm. Readings made at end of 6 seconds vary by 0.4 per cent from mean; 20 ohms in series with the galvanometer. Temperature sensitiveness $= 5° \times 10^{-6}$.

The first test made was to determine whether the rotating disk (30 cm. diameter, 1.3 m. from the bolometer) affected the instrument; and it was found that the resulting deflections 1 to 2 mm. were no larger than those due to stray radiation reflected from the stationary disk. A heavy black cardboard shield was then placed between the bolometer and the disk (0.5 m. from the disk) and similar screens were placed around the source, which was 2 m. from the bolometer. No radiation was detected from the stationary disk, whether the open or closed part of the disk faced the bolometer; but unfortunately this test was not made for the moving disk. The disk with the 240° opening gave values 0.5 per cent too high (see table IX). The results with the 120° disk (6 openings of 20° each) were in still greater error. The space between the bolometer and the shield was then entirely inclosed, and with the disk close to the opening (7×10 cm.) in the shield the discrepancy became still greater. It was then found that the increased transmission is due to the moving disk and depended upon the distance of the disk from the screen.

It was further shown that the transmission was proportional to the speed, so that the 240° disk (true transmission 66.827 per cent[1]) gave

[1] These disks and their constants were supplied by Dr. Hyde. Bureau of Standards, Bulletin, 2, p. 1, 1906.

values from 69.3 to 77.2 per cent. In fig. 105 are plotted the galvanometer deflections for different distances of the disk (abscissæ) from the screen. The latter was 80 cm. (source at 2 m.) from the bolometer, and had an opening in it which was the size of the openings in the sectored disk. No radiation was observed from the stationary disk, nor from the shields back of it when the open sector was before the bolometer. The speed of the disk was such as is used in photometry, and was kept constant for each series of observations. In the lower curve for the 240° disk the speed was slow and there was a flicker on viewing it. The curves show that the maximum radiation occurs when the disk is about 6 cm. from the shield; and it disappears immediately on stopping the disk.

TABLE IX. — RELIABILITY OF BOLOMETER MEASUREMENTS.

Direct deflection. *a*	Deflection with disk. *a*	Ratio.	Direct deflection. *a*	Deflection with disk. *a*	Ratio.
Disk opening, 240° = 66.827.			Disk opening, 120° = 33.406.		
9.42 cm.	6.33 cm.	*b* 67.23	15.82	5.65	*e* 35.70
9.35	6.28	*b* 67.25	11.56	4.14	*f* 35.75
11.82	7.95	*b* 67.25	12.31	4.28	*g* 34.8
9.11	6.12	*b* 67.2	30.40	10.53	*h* 34.7
8.94	6.04	*c* 67.5	13.75	4.70	*i* 34.5
13.31	8.99	*c* 67.6	14.15	4.75	33.56
			17.04	5.68	33.38
Disk opening, 180° = 50.125.					
17.17 cm.	8.65	*d* 50.37			
17.21	8.64	*d* 50.20			

a Mean of 6 to 10 readings.

b Galvanometer period 8 seconds, vibration undamped; 20 ohms in series with galvanometer. Temperature sensitiveness = $6° \times 10^{-5}$ C. High values due to radiation from moving disk, which is 0.5 m. from screen.

c Galvanometer period 14 seconds and vibration just damped. Temperature sensitiveness = $1°.2 \times 10^{-5}$ C.

d Nernst heater on 98 volts at 1 m. from bolometer. Galvanometer period 8 seconds. 30 ohms in series with galvanometer. Total deflection about 80 cm. Individual deflections vary 0.2 to 0.5 per cent from mean.

e Galvanometer period 14 seconds.

f Galvanometer period 8 seconds. Disk better shielded than in previous experiments and closer to screen — 6 cm. from it. Heater 150 cm. from bolometer; screen at 80 cm.

g 14 ohms in galvanometer circuit. Galvanometer period 14 seconds. Nernst heater on 74 volts.

h No resistance in galvanometer circuit; results show that high value is not due to lack of proportionality of galvanometer deflections.

i Nernst heater on 95 volts. 20 ohms in galvanometer circuit. Total deflection about 45 cm.

The motor was run continuously for a complete series of measurements and no deflections greater than 1 to 2 mm. were observed from it or the disk, immediately after stopping the rotation. In these tests the motor was shielded from the bolometer. On removing the shield and the disk and on running the motor the deflections were from 1 to 3 mm. The whole shows that the sectored disk is not as applicable as one would suppose, unless one determines the corrections which in two series of experiments were found to be in very close agreement.[1] In the present curves

[1] The sector was rotated at a higher speed than actually required with a bolometer. By means of suitable pulleys the speed may be reduced to perhaps $\frac{1}{5}\frac{1}{0}$ that used in the present test, which would decrease the errors.

the galvanometer was at its full sensitiveness — no resistance in series — so that in the actual experiments (table IX) the error was less exaggerated. For the 240° disk where the error in the deflections was only 1 or 2 mm. the correction reduces the observed values close to the true one.

From the consistency of the ratios in each series, which is of the order of 0.2 to 0.3 per cent, it will be noticed that the bolometer is a very reliable instrument in spite of its mechanical weakness.

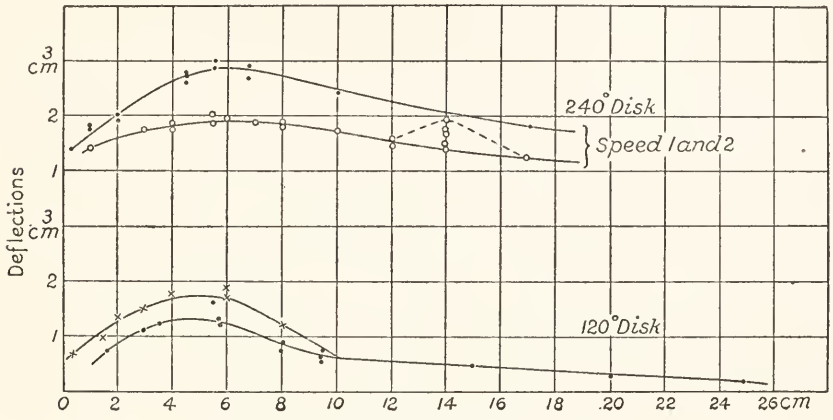

FIG. 105. — Radiation due to rotating sectored disk.

VI. SUMMARY.

The present paper deals with four instruments for measuring radiant energy, viz, the radiomicrometer, the linear thermopile, the radiometer, and the bolometer with its auxiliary galvanometer.

As a result of this historical inquiry and by experiment it was shown that the radiomicrometer is capable of great improvement, by reducing its weight, by lengthening its period, and by placing it in a vacuum. It was further shown that on account of para- and dia-magnetism the sensitiveness of the radiomicrometer is very limited, perhaps only a fifth of the best bolometers described.

It was also shown that the Rubens thermopile is as sensitive as the best bolometer, and that its heat capacity can be greatly reduced by using thinner (0.06 to 0.08 mm. diameter) wires, which are made shorter, thus keeping the resistance low. The computed errors due to the Peltier effect are about 1 part in 300. The thermopile is not so well adapted as is the bolometer for instantaneous registration of radiant energy and it does not admit so great a range in variation of sensibility; but, on account of its greater steadiness, it commends itself for measuring very weak sources of radiation, *e.g.*, the extreme ultra-violet and infra-red region of the spectrum.

By a direct comparison it was shown that the radiometer can be made just as sensitive as the bolometer, but its period will be much longer. It

was found that the radiometer is not selective in its action, and, hence, that it can be used for measuring ultra-violet radiation. The main objection to the use of a radiometer is its long period; but, since it is easily shielded from temperature changes, and since it is not subject to magnetic perturbations, this long period is of minor importance so long as we are dealing with a constant source of radiation. In spectrum energy work its usefulness is limited to the region in which the window is transparent — to 20 μ and from 40 to 60 μ by using quartz. The fact that the deflections of the radiometer can not be obtained in absolute measure is a minor objection, since in but few cases (thus far at least) has it been necessary to thus obtain the deflections. The action of a radiometer is somewhat analogous to a photographic plate, in that it will detect weak radiation, provided one can wait for it, and, on account of its great steadiness, is, of all the instruments considered, probably the best adapted in searching for infra-red fluorescence.

A bolometer installation is so distributed that it is difficult to shield from temperature changes. In spite of its small heat capacity the bolometer has a "drift" due to a slow and unequal warming of the strips. Air-currents which result from the hot bolometer strips also cause a variation in the deflections of the auxiliary galvanometer. Nevertheless, despite these defects it is the quickest acting of the four instruments considered, and is the best adapted for registering the energy radiated from a rapidly changing source. For precision work it is necessary to keep the bolometer balanced to less than 1 cm. deflection.

The auxiliary galvanometer is the main source of weakness in measuring radiant energy, and in places subject to great magnetic perturbations a period greater than 5 seconds, single swing is to be avoided. Hence, although a greater sensitiveness is possible, the working sensibility of the various galvanometers studied is of the order of $i = 2 \times 10^{-10}$ ampere per millimeter deflection on a scale at 1 m. Under these conditions the various bolometers used were (as a fair estimate of the recorded data) sensitive to a temperature difference of $4^{\circ} \times 10^{-5}$ to $5^{\circ} \times 10^{-6}$ per mm. deflection, on a scale of 1 m. The galvanometer sensibility was found to be closely proportional to the period.

A direct comparison of the thermopile and the bolometer shows that there is little preference, other than a personal one, in these two instruments.

The use of a rotating sectored disk for reducing the intensity of the source is liable to introduce errors, which must be taken into account.

APPENDIX III.

ADDITIONAL DATA ON SELECTIVE REFLECTION AS A FUNCTION OF THE ATOMIC WEIGHT OF THE BASE.

As this work goes to press the experiments of Morse[1] have been published, and since it contains considerable new data for the region of the spectrum from 10 to 15 μ, it is included here for the sake of completeness.

In that paper considerable comment is made upon the fact that the writer (see Carnegie Publication No. 65) missed the reflection bands in calcite and in magnesite, previously found by Aschkinass at 11 to 12 μ. In reply it may be stated that these two substances were examined in the preliminary work on reflection spectra, in order to get a check on the calibration; and, on finding the reflected energy very weak, no attempt was made to locate the bands known to be at 11 to 12 μ. In this work a Rubens thermopile (heavy wires) was used, which was sluggish and was disturbed by air-currents. Although the sensibility was higher than in the radiometer previously used, the small deflections were not so reliable and no attempt was made to locate weak reflection bands beyond 11 μ, such as are found in the carbonates. This demonstrates the superiority of the radiometer for measuring weak radiation.

The investigation of weak reflection spectra in the extreme infra-red is accomplished under great difficulties, and Morse has done an excellent service in obtaining data in this region of the spectrum. He used a 35 cm. focal length mirror spectrometer as compared with the writer's 52 cm. focal length mirrors. In the larger spectrometer the energy in the spectrum is much weaker, while the resolution is greater. The shorter focus does not militate against the results, however, which show that the simple atomic weight relation among the carbonates found by the writer at 6 to 8 μ holds for the long wave-lengths at 11 to 15 μ, where the dispersion is considerably greater. The writer found the reflection band of the carbonates at 6 μ very complex (see Chapter III) and it would be interesting to learn whether the bands at 11.4 to 15 μ are likewise. In table X are given the maxima of the reflection bands of the carbonates examined by Morse. It contains one new substance, $MnCO_3$, not examined by the writer. The values of the maxima of the first band are not always in agreement, but this appears to be due to the difference in resolving power of the two instruments. In fig. 43 are plotted the wave-lengths of the

[1] L. B. Morse: Astrophys. Jour., 26, p. 225, 1907.

reflection maxima of the bands at 11.5 and 14.5 μ against the atomic weight of the base. From this it will be seen that the rate of shift of the band with increase in atomic weight of the base is greater for the bands at 11.5 and 14.5 μ than for those at 6.6 and 7.0 μ, just as was found for the bands of the sulphates at 4.6 μ, at 6.2 to 6.6 μ, and at 8.2 to 9.3 μ (see figs. 44 and 45).

TABLE X.

Substance.	Chemical composition.	Atomic weight of base.	Reflection maxima.		
			Band 1.	Band 2.	Band 3.
Magnesite	$MgCO_3$	24.2	6.5 μ	11.2 μ	13.9 μ
Calcite	$CaCO_3$	39.7	6.6	11.31	14.2
Aragonite	$CaCO_3$	39.7	6.65	11.55	14.2
Rhodochrosite	$MnCO_3$	54.6	6.63	11.47+	14.0—
Siderite	$FeCO_3$	55.5	6.60	11.47—	13.9—
Smithsonite	$ZnCO_3$	64.9	6.7	11.38	13.6
Strontianite	$SrCO_3$	86.9	6.76	11.56	14.37
Witherite	$BaCO_3$	136.4	6.86	11.60	14.5
Cerussite	$PbCO_3$	205.4	7.2	11.94	14.8

By arbitrarily selecting KNO_3 and $AgNO_3$ from the nitrates, Morse found the line drawn through the maxima of the reflection bands was "approximately parallel" to those of the carbonates (see fig. 43). Moreover, the line drawn through the maxima of the sulphates, at 8.6 to 9 μ, is also closely parallel with those of the carbonates. From this he was led to suspect that the shift of the band with increase in the atomic weight of the base is of the same order of magnitude in carbonates, nitrates, and sulphates. If the data had been plotted to a larger scale, as the accuracy of the values of the maxima seem to permit, then the lines would not even be approximately parallel, as will be noticed in figs. 43 and 44.

After examining the reflection and transmission spectra, one or both, of over 300 substances, the observations lying in the region of the spectrum from 0.5 to 30+ μ, I have found that it is an easy matter to work out all sorts of fantastic relations, only to learn, after gathering more data, that the whole thing was an illusion. For this reason it seems to me that the linear relation between the weight of the element, combined with equal amounts of oxygen in the acid radical found by Morse by arbitrarily selecting maxima of reflection bands, is misleading. From the earliest work of Abney and Festing to the latest (theoretical) work of Einstein, it has been generally accepted that oxygen is the active element in causing (at least in "sharpening") certain bands, just as sulphur has been found quite inactive. The great groups of chemically related compounds have been found to have similar absorption and reflection spectra, but no simple relation could be established between the spectra of the groups of compounds. The present simple relation results from selecting particular reflection bands found in certain carbonates, nitrates, sulphates, and sili-

cates. Hence, the selection of KNO_3 (max. at 7.1 μ) from the nitrates by Morse seems arbitrary, for Pfund (*loc. cit.*, see Carnegie Publication No. 65) has given a large number of nitrates which have a band in common at 7.45 μ. This seems to be a characteristic band of the nitrates, and $AgNO_3$ might have been selected instead of KNO_3. A characteristic band of the sulphates appears to be at 9.1 μ (harmonic with the one at 4.55 μ), while Morse selected a less frequent one at 8.6 μ. From the silicates, $MgSiO_3$, with an insignificant band at 9.1 μ, was selected, while Na_2SiO_3, with a sharper band at 9.9 μ, and Zn_2SiO_4, with a group of still more intense bands at 10.1, 10.6, and 11 μ, respectively, were not considered.

In $PbMO_4$ the maxima lie in the region of 11.75 and 13 μ, while in $CaWO_4$ there is a large reflection band with maxima at about 11.4, 11.9, and 12.5 μ, respectively. These data including Morse's are plotted in fig. 106 and tabulated in table XI, from which it will be observed that

TABLE XI.

Substance.	Chemical formula.	Atomic weight of base.	Weight with 48 gr. of O.	Position of band.
Calcite	$CaCO_3$	39.7	12 gr. of C	6.6 μ
Potassium Nitrate	KNO_3	38.9	14 gr. of N	7.15 (7.05)
Anhydrite	$CaSO_4$	39.7	24 gr. of S	8.6
Enstatite	$MgSiO_3$	24.2	28 gr. of Si	9.1
Zircon	$ZrSiO_4$	90.6	28 gr. of Si	10, 10.6, 11 μ
Wulfenite	$PbMoO_4$	206.9	72 gr. of M	11.75, 13
Scheelite	$CaWO_4$	39.7	138 gr. of W	11.4, 11.9, 12.5

the graph is not a straight line, and that if any relation exists it is a very complex curve, showing that for the region up to 10 μ the atomic weight of the element in the acid radical has a great effect in shifting the maximum, while beyond this point the atomic weight of the element united with oxygen is of minor importance. In fact, the base and the element united with the oxygen in the acid radical seem to influence each other.

As an illustration of the arbitrariness in selecting bands to establish relations like the aforesaid, calcite ($CaCO_3$) may be noticed, in which the reflection band is complex with maxima at 6.4 (?), 6.5, 6.6, and 7 μ, while in its isomer, aragonite, the maxima are at 6.4 (?), 6.52, 6.74, and 7 (?) μ. In $SrCO_3$ the band with a maximum at 6.67 μ could not be resolved even with a fluorite prism. Hence, one is at a loss to know which band (at 6 to 7 μ) to select from the carbonates to compare with the sulphates, nitrates, and silicates. On the other hand, in the carbonates and in the sulphates the maxima of the bands have been plotted in their order of occurrence, which would seem to eliminate personal bias in the selection of maxima. From this it would appear that the simple, linear relation between the atomic weight of the base and the maxima of the reflection

bands in the carbonates and in the sulphates is in agreement, at least as a first approximation. Even with these data at hand, speculation in regard to dynamical relations among atoms in the molecules had better be postponed until more data have been procured.

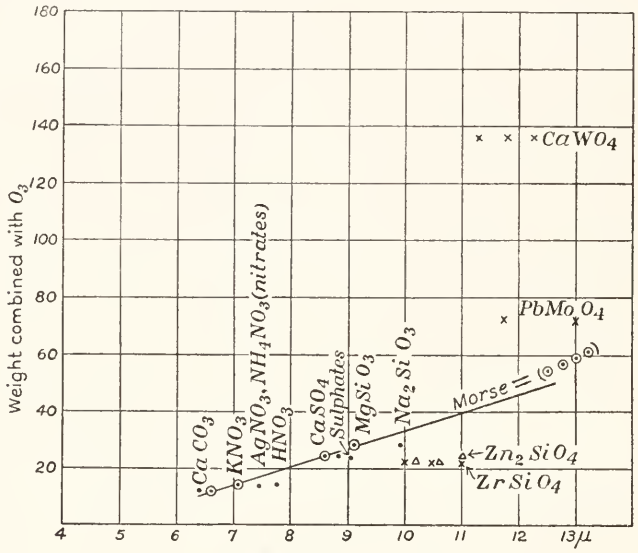

Fig. 106. — Maxima of reflection bands.

The data on the reflection bands of the carbonates at 11 to 15 μ is of interest in connection with the question of the value of the extinction coefficient necessary to give rise to selective reflection. In Carnegie Publication No. 65, page 70, is given the transmission band of a thin section of calcite, from which it will be observed that the absorption band at 11.4 μ coincides with the band found by reflection. It would seem desirable to examine the transmission of thin sections of carbonates in this region of the spectrum, using polarized energy, to compare with the intensity of the bands found by reflection. The reflection bands at 14 μ were frequently found to be extremely weak, and in view of the importance of the bearing of the results upon the whole subject, it seems highly desirable to examine the transmission spectra of thin sections of these minerals (using preferably polarized energy), to verify the aforesaid observations. (See foot note on page 30.)

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ADDENDUM.

Mr. Morse has recently presented "Additional observations on the selective reflection of salts of oxygen acids" (Washington meeting, American Physical Society, April, 1908). He chose substances in which the "weight of the acid-forming element is not greater than the weight of the oxygen with which it is combined." These substances are: $CaCO_3$ with a reflection maximum at 6.6 μ; KNO_3 at 7.1 μ; $AgNO_3$ at 8 μ; $CaSO_4$ at 8.6 μ; $KClO_4$ at 9 μ; $CaSiO_3$ at 9.2 μ; $KClO_3$ at 9.9 μ; $KMnO_4$ at 10.9 μ; $PbCrO_4$ at 11.5 μ; and $CaTiO_3$ at 14.2 μ. These maxima lie close to the line drawn through them, when plotted against the weight of the oxygen. He excluded $PbMO_4$, $CaWO_4$, etc., because the weight of the acid-forming element is greater than that of the oxygen present. Of course, if we admit the validity of such a procedure the rule is proven; but a rule loaded down with exceptions can not prove satisfactory, and much as all spectroscopists wish to establish such a simple relation *between spectra of different groups of compounds*, it should be along lines of less arbitrary elimination.

On the other hand, this simple atomic-weight relation seems to hold *for substances belonging to the same group of compounds*, even for remote parts of the infra-red spectrum, as was shown by Nichols and Day (Washington meeting, American Physical Society, April, 1908). They found a band of residual rays in $SrCO_3$ at 43.2 μ and in $BaCO_3$ at 46.5 μ, for the carbonates (see fig. 45).

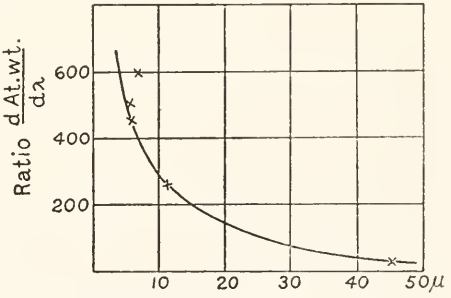

FIG. 107. — Mean position of groups of residual rays.

If we take the ratio of the increase in atomic weight of the base to the position of the maximum, as read from the graphs in figs. 43 to 45, the value for the group of bands at 6.5 μ is about 500 to 1, at 11.5 μ it is 260 to 1, and at 45 μ it is 20 to 1. The graph (fig. 107) of these values appears to be an hyperbola. If such a relation really exists and if the carbonates have a band in the region of 30 μ, corresponding to the $CaCO_3$ and $MgCO_3$ bands, then the aforesaid ratio of atomic weight to position of the maximum is about 90 to 1, and one would expect to find a maximum for $PbCO_3$ at 31.5 μ and $SrCO_3$ at 30 μ. However, from the variation in complexity of the bands at 6 to 7 μ and in intensity of the bands at 11 to 14 μ, it is evident that it is use-

less to attempt to predict their behavior in the remote infra-red. On the whole, the present data indicate that the greater the wave-length of the maximum the greater the shift of that maximum with increase in atomic weight of the base.

The latest conclusion (Morse, Phys. Rev. 26, p. 526, 1908) is that "present data do not form any reasonable basis for assuming that all the reflection bands in even the simpler oxygen acids are connected with each other by such a simple relation as that found to hold roughly for the first bands, and which may be found to hold also for the second bands in the salts examined."

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SUPPLEMENTARY INVESTIGATIONS
OF
INFRA-RED SPECTRA

Part V—Infra-Red Reflection Spectra
Part VI—Infra-Red Transmission Spectra
Part VII—Infra-Red Emission Spectra

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